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Microgravity Science and Applications Program Tasks

1990 Revision

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NASA Technical Memorandum 4284

Microgravity Science and Applications Program Tasks

1990 Revision

*NASA Office of Space Science and Applications
Washington, D.C.*



National Aeronautics and
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I. INTRODUCTION

NASA TECHNICAL MEMORANDUM

I. INTRODUCTION

The Microgravity Science and Applications (MSA) Program is directed toward research in the science and technology of processing materials under conditions of low gravity to provide a detailed examination of the constraints imposed by gravitational forces on Earth. The program is expected to lead, ultimately, to the development of new materials and processes in commercial applications adding to this nation's technological base. The research studies emphasize the selected materials and processes that will best elucidate the limitations due to gravity and demonstrate the enhanced sensitivity of control of processes that may be provided by the weightless environment of space. Primary effort will be devoted to a comprehensive study of the specific areas of research which revealed potential value in the initial investigations of the previous decades. Examples of previous process research include growth of crystals and directional solidification of metals in the quiescent conditions in which gravitational fluid flow is eliminated; containerless processing of reactive materials to eliminate reactions with the container and to provide geometrical control of the product; synthesis and separation of biological materials in weightlessness to reduce heat and mass transfer problems associated with sedimentation and buoyancy effects; identification of high vacuum characterization associated with an orbiting wake shield; and minimal knowledge of terrestrial processing methods.

Additional effort will be devoted to identifying the special requirements which drive the design of hardware to reduce the risk in future developments. Examples of current hardware studies are acoustic, electromagnetic, and electro-static containerless processing modules and electrophoresis separation devices.

The current emphasis on fundamental processing science and technology in selected areas will continue as the Microgravity Science and Applications Program addresses problems of interest to the public and private commercial sectors which can be resolved by recourse to the space environment.

Emphasis will be placed on the expansion of currently funded activities for ground-based and space flight investigations to maximize the outputs from these opportunities. Initiatives requiring new hardware will be encouraged at a low level until funds can be made available. The expansion of current efforts is occurring as a result of focusing support for current space flight investigations on forming facility experiment teams to provide advice and identify future involvement. Emphasis has been placed on experiments involving the Materials Experiment Assembly and Mid-deck experiments on the Space Shuttle.

The Microgravity Science and Applications Program Task Document covers the period of January 1990 - December 1990. The document includes research projects now being funded by the Office of Space Sciences and Applications, Microgravity Science and Applications Division, NASA Headquarters.

The Microgravity Science and Applications Division wishes to thank the Universities Space Research Association (USRA) and in particular Ms. Elizabeth Pentecost, for her efforts in the compilation and publication of this report.

II. TASKS

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A. GROUND BASED EXPERIMENTS

1. ELECTRONIC MATERIALS

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Growth of Zinc Selenide Crystals by Physical Vapor Transport in Microgravity

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NAG8-767 (NASA Contact: Dr. S. L. Lehoczky, MSFC)
April 1989 - March 1992

Objectives: The overall objective of this program is to contribute to the understanding of the physical vapor transport (PVT) crystal growth method for possible future processing of II-VI compounds under low gravity conditions. As a basis, we strive to determine the optimum conditions for the PVT growth of single crystals of zinc selenide of good optical quality under normal gravity. A long-term objective is to extend the PVT method to the growth of mixed systems, such as ZnSe-ZnS. We aim to develop a research program with supplementary efforts in crystal growth, structural and optical characterization of the crystals, compositional characterization of the vapors and solids involved in the process, and in the numerical modelling of transport rates.

Research Task Description: Towards these objectives we are pursuing the following tasks:

- Vacuum conditioning and prepurification of starting materials to maximize transport rates. Since optimal transport rates can only be expected for quasi-congruent vapor composition, the starting material is preconditioned by a free sublimation that reduces volatile impurity concentrations and shifts in stoichiometry with respect to congruency.
- Vapor transport and crystal growth experiments in closed ampoules: this entails a study of nucleation distribution, transport rates and crystal habit as a function of ampoule dimensions and shape, and external temperature distribution.
- Vapor transport and crystal growth experiments in effusive ampoules, in order to provide for some uncoupling between transport rates and temperature distribution, and for further removal of incongruent vapor components during transport.
- Characterization of crystals by optical microscopy and scanning electron microscopy of etched and unetched crystal faces to determine the concentrations of dislocations, twin boundaries and possible precipitates. Infrared absorption spectra will be obtained for the best samples.
- Mass spectroscopic studies of the outgassing behavior of starting materials and silica ampoule material in order to provide guidance for the development of bake-out and seal-off procedures that will minimize the amount of impurities introduced into the vapor and, thus, potentially into the crystal.
- Numerical modeling of physical vapor transport for various conditions in temperature distribution, impurity or inert gas pressure, and vapor pressure differences between source and crystal interfaces. As our earlier efforts with PVT modeling and laser Doppler anemometry revealed geometrically rather complex transport flux distributions, realistic results can only be expected from 3-D models.

Progress to Date: The experimental setups for high-vacuum preconditioning, ampoule sealing, PVT crystal growth (including two three-zone furnaces, both with heat pipes), effusive ampoule vapor transport, etching and optical microscopy, mass spectroscopy (employing a high temperature effusion technique) have been completed and modified for the use with or the characterization of ZnSe.

About 20 growth runs in closed ampoules have been performed. With the evolution of optimal bakout and preconditioning procedures our transport rates in closed ampoules have recently increased to about 900 mg/day (18g/20 days). The crystal boule dimensions have increased to 2cm x 2.5cm, with only a few single crystalline grains per boule. While earlier boules showed extensive twinning and dislocation densities ranging from 10^4 - $10^7/\text{cm}^2$, a considerable reduction of defect densities can probably be achieved through more advantageous post-growth cooling programs. On samples where absorption spectra have been made, the IR transmission is greater than 80% from 1.8 to 15 microns. Electrical resistivity measurements indicated semi-insulating material.

The first few unseeded growth runs with the effusive ampoule technique, that were conducted recently, were also very promising and yielded growth rates of several 0.1 mm/hr. Here future work will concentrate on seeding and advantageous cooling of large area seed plates.

The feasibility of the mass spectroscopic characterization of the outgassing products of silica ampoule material has been demonstrated and significant amounts of CO have been detected. These initial runs have revealed some incompatibility between SiO_2 and the BN used for the effusion cell; hence, future runs will be conducted with a platinum cell.

In the 3-D modelling of PVT rates we have encountered great difficulties. A comparison between unusually well characterized experimental transport rates, obtained in our group earlier, and numerical results revealed the inability of most commercially available 3-D numerical codes to handle the concentration boundary conditions associated with PVT. Close interaction with two code-development efforts, however, let us believe, that we will be able to satisfactorily tackle this problem in the near future.

Presentations

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Memory Effects in Organometallic Molecular Beam Epitaxy

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In the first year of funding the research on II-IV-V₂ heterostructures focussed onto ZnGeP₂-Ge and ZnGeP₂-ZnSiP₂-Ge alloys grown on GaP and Si substrates. Lattice fringes were revealed by HREM that show the nearly perfect matching of the lattice constants of the materials combinations used in this work. Double heterostructures were achieved on GaP(001) substrates, growing 1000Å thick layers of ZnGeP₂-Ge sandwiched in between epitaxial layers of GaP. To our knowledge this is the first time that double heterostructures have been produced between II-IV-V₂ and III-V materials. However, SIMS profiling shows that the GaP front layer is heavily Zn doped due to memory effects, the prevention of which is the final goal of a space based experiment in NASA's future SURF facility. Based on our preliminary results we expect that sharp multiple and single quantum well heterostructures can be realized in this novel materials combination that integrates tetrahedrally coordinated cubic and birefringent tetragonal structures of high nonlinear optical figure of merit. Also, ZnSiP₂-ZnGeP₂ alloys have been grown with excellent perfection on (001) GaP substrates up to 5% ZnSiP₂ in the alloy as revealed by cross section TEM. Using a rf plasma source, we have been able recently to produce highly textured crystalline GaN on sapphire by plasma enhanced OMCVD at 500°C. This work is presently being extended to phosphides. We are interested in the above wide band gap materials because of their potential opto-electronic applications in the blue to near UV wavelength region. Future work will concentrate on the development of solid source materials for the growth of the above pnictide heterostructures and the extension of our work to chalcogenides, i.e. I-III-VI₂/II-VI and I-III-VI₂/IV heterostructures. One PhD thesis and a masters thesis based on some of the above research have been completed and 2 PhD theses are presently being continued in this program.

Publications

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Electronic Materials

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The objective of this project is to develop a synergistic approach to crystal growth of electronic materials combining both theoretical and experimental techniques. Activities in the arena of electronic materials fall into four categories: growth of optoelectronic salts, study of the interaction of radiation and convection during physical vapor transport, modelling of crystal growth processes, e.g. GaAs Bridgman growth, and study of residual acceleration effects.

Salts having favorable infrared transmission characteristics have been under joint study by researchers from Westinghouse and Lewis. Both physical vapor transport and melt growth by Bridgman techniques have been used, the first for Hg_2Cl_2 , the second for PbCl_2 and PbBr_2 . All three of these materials have been identified by Westinghouse for their potential use in advanced optoelectronic devices. Preliminary experiments have delineated thermal gradient and growth rate regimes for quality crystal growth. Based on work performed at Lewis and at Westinghouse a flight proposal was prepared by Westinghouse in response to the Announcement of Opportunity. Dr. Walter Duval is serving as the project scientist for this accepted proposal. The contributions of the Lewis team, especially Dr. Duval, to the Westinghouse effort have been formally recognized in a letter from Westinghouse to Lewis Center Director, Lawrence J. Ross.

Because the salts are transparent themselves and because they can be grown in quartz (transparent) crucibles radiative heat transfer must be considered to understand their crystal growth. When modelling growth of opaque materials, schemes very similar to traditional finite element modelling of stress fields may be used. Here each element interacts only with its adjacent neighbors. But when transparent or semitransparent materials are involved, an element may exchange energy with a distant element, greatly complicating the mathematics. Radiative heat transfer is often ignored in modelling, even in vapor transport where evaporating and condensing surfaces are within direct view. While this may be reasonable for low temperature work, such as the vapor transport of organic molecules, it is not appropriate for the high temperatures at which semiconductors and salts are grown. (Note that ignoring radiative transport is not appropriate for organic materials transport when temperature gradients and temperature differences are high as in the 3M PVTOS experiments.) At Lewis we have begun to include radiative transfer in treatment of physical vapor transport. First results indicate that interface shape is influenced by radiation; the influence is slight for earthbound growth, but becomes more important in space as convection decreases. Dr. Mohammad Kassemi has led this work; he has presented a paper describing early results at the Reno AIAA meeting.

Modeling has been extended at Lewis to the GaAs growth experiment planned by GTE. Their approach is to employ a GAS canister to hold their own fairly simple power down furnaces. In a GTE furnace, about three inches of a four inch sample are to be melted then regrown to study solute redistribution and crystal growth in microgravity. The sample and its dual walled (quartz and BN) crucible have been modelled and growth has been simulated for various acceleration environments, including one-g, Shuttle, sounding rocket, and aircraft flight. For samples of the diameter and viscosity of the GTE experiment, the results indicate that aircraft offer insufficient time at low acceleration to allow damping of initial convection. Rocket flight would allow damping dominated by diffusion for the planned growth rate. The growth interface is predicted to be gently curved. A broadly applicable, simple formula for estimating the time required for an initial annular convection cell to damp to a desired fraction of its original value was obtained. The equation, in dimensional units, is

$$t \approx 0.0291n(1-FR)^* r^2/v$$

where FR is the fraction remaining of the original convection velocity, r is the ampoule radius, and v is the melt kinematic viscosity. The relation was obtained considering several independent numerical studies of directional solidification.

Starting with the work on DMOS, 3M's flight experiment for diffusive growth of organic crystals, Lewis researchers have been developing mathematical tools for investigating convective mixing in microgravity environments. Both steady and time varying accelerations have been examined. It has been found that completely reversed accelerations, i.e. g-jitter, can cause complete mixing at appropriate interrelations of frequency, amplitude, viscosity, density, and density difference. Steady acceleration is much less effective at mixing, though it can cause bulk fluid flow. Developed for understanding the DMOS experiments, these tools are now available to other researchers through Lewis. In the past year the modelling associated with the question of varying accelerations has been graphically displayed on video by Dr. Walter Duval; copies may be obtained from him.

For the past two years the efforts of the Lewis group have been augmented by Dr. Christophe Mennetrier, a post doctoral from France; he has investigated the role of crucible inclination during the physical vapor transport of a heavy molecule in a lighter diluent gas. His results, again presented on video, show that even slight inclinations lead to nonaxisymmetric flows that the nominally stable orientation of hot end elevated is not necessarily stable. In later work, Christophe Mennetrier, Mohammad Kassemi, and Henry de Groh combined forces to study the alteration of natural convective flows by radiative heat transfer.

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Growth of Solid Solution Crystals

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The major objective of this research is to establish the limitations imposed by gravity during growth on the quality of bulk solid solution semiconducting crystals. An important goal is to explore the possible advantages of growth in the absence of gravity. The alloy system being investigated is $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ with x-values appropriate for infrared detector applications in the 8 to 14 μm wavelength region. Both melt and Te-solvent growth, as well as growth in a magnetic field, are being considered. The study consists of an extensive ground-based experimental and theoretical research effort required to define the optimum experimental parameters of the planned flight experiments. $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ is representative of several II-VI alloys which have electrical and optical properties that can be compositionally tuned to meet a wide range of technological applications to optical computing and communications as well as the national defense.

A series of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ alloy ingots ($0 \leq x \leq 0.6$) has been grown from pseudobinary melts by a vertical Bridgman-Stockbarger method using a wide range of growth rates and thermal conditions. Precision measurements were performed on the ingots to establish compositional distributions for the ingots. Growth rates and thermal conditions required to obtain the desired growth interface shape have been established for the system.

To assist the interpretation of the results and the selection of optimum in-flight growth parameters, the pseudobinary phase diagram ($0 \leq x \leq 1$), liquid and thermal diffusivities ($0 \leq x \leq 0.3$), and the specific columns as a function of temperature ($0 \leq x \leq 0.15$) have been measured. From these measurements and other available data, the heat capacity, enthalpy of mixing, and the thermal conductivity of pseudobinary melts have been calculated using a regular associates solution model for the liquid phase. A one-dimensional diffusion model that treats the variation of the interface temperature, interface segregation coefficient, and growth velocity has been used to establish effective diffusion constants for the alloy system. Theoretical models have been developed for the temperature distribution and the axial and radial compositional redistribution during directional solidification of the alloys. These models are sufficiently accurate that they will be used along with the experimental results to select parameters for the first flight experiment to be flown on the USMP-2 mission using the Advanced Automatic Directional Solidification Furnace (AADSf).

A microscopic model for the calculation of charge-carrier concentration, Fermi energy, and conduction-electron mobility as functions of x, temperature, and both ionized and neutral defect densities has been developed. For selected samples, measurements were performed of electron concentration and mobility from 10-300K. The experimental data were in reasonably good agreement with theory and were successfully analyzed to obtain donor and acceptor concentrations for various processing conditions.

The crystal growth studies have been extended to include additional Hg-based II-VI alloys. Large crystal ingots of HgZnTe and HgZnSe have been successfully grown by the Bridgman-Stockbarger method and a detailed theoretical analysis of the measured axial compositional distribution in the ingots was used to establish for the first time effective HgTe-ZnTe and HgSe-ZnSe interdiffusion coefficients for the molten alloys. Both the Te and Se-based alloys showed

improvements in lattice strength resulting from the substitution of Zn into the respective Cd lattice sites. In particular, measured electrical and optical properties, thus providing the first direct experimental confirmation for predicted improvement in lattice stability against point-defect formation resulting from Zn-additions.

Microhardness measurements were performed on selected wafers cut from the various alloy crystals. For each alloy, measurements were made for several alloy compositions. The microhardness results support the above conclusions. Sample cartridges needed for the integration of the samples into the space flight hardware are being developed. $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ between 2 and 5 kg. Precise compositional mapping of the ingots showed that the fields had significant effect on the composition for the entire field range.

The development and fabrication of the AADSF flight unit and a Ground Control Experiment Laboratory unit have nearly completed and are being readied for flight qualification testing.

Publications

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Growth Kinetics of Physical Vapor Transport Processes, Crystal Growth of an Opto-Electronic Material, Mercurous Chloride

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Objectives: Mercurous chloride, currently under intense development for device application, is both a commercially important acousto-optical material and an ideal model for study of microgravity effects on the Physical Vapor Transport crystal growth Process. The objective of the program is to demonstrate increased crystal homogeneity and reduced optical scatter by employing the micro-gravity environment in space to minimize harmful convective effects during crystal growth. The ground based experiment will provide informations to grow the best possible optical quality crystals and identify the conditions under which microgravity environment of space might be employed to change the convection conditions during the crystal growth.

Research Task Description: A high degree of uniformity in refractive index is essential to achieve maximum device efficiency. This will also provide a desirable low optical and acoustic attenuation. In the earth grown crystals, thermal and solutal convection during vapor transport can degrade the chemical and optical homogeneity of the crystals significantly. For this reason we are measuring the crystal growth rate at various g-vectors and at various aspect ratio. This provides different convective environments during crystal growth which ultimately affects the homogeneity. The crystal homogeneity is evaluated by transparency and scattering measurements.

Progress to Date: Mercurous chloride is an extremely anisotropic material. The growth rate depends on orientation of crystal, purity of source material, thermal conditions, g-vector and aspect ratio. To achieve the objectives of the present program, we are measuring growth rate of crystals at various g-vectors in a cylindrical container. The source material was purified and prepared in the form of solid cartridge to control the aspect ratio (transport length and radius of crystal). The temperature distribution of the furnace was also kept identical for all the runs. All the crystals were grown in [110] orientation to avoid the anisotropy effect. Preliminary data showed variation in growth rate of crystals as the function of orientation with respect to gravity vector. Similar behavior was observed when we changed the convective conditions by changing the aspect ratio during the transport process. Data from this experiment will be used to develop a flight experiment on PVT growth of mercurous chloride.

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Casting of Solid Solution Semiconducting Alloys

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Objectives: The primary objective of this research study is to establish the effects of the processing environment, including gravitational and magnetic fields, during the casting of semiconducting, solid solution crystals on the compositional, metallurgical, electrical, and optical characteristics of the crystals. Specific goals include the use of the results to gain insight into the nature of the fluid flows in these materials and to distinguish between gravity and non-gravity driven fluid effects.

Research Task Description: The investigation is intended to provide a 1-g data base and to define a flight experiment that will establish the effects of gravity during rapid solidification of semiconducting, solid solution crystals. The strategy includes casting, post-casting annealing under a variety of conditions, and characterization of II-VI solid solution semiconducting alloys (e.g., $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$). Parameters to be varied during casting include the direction of the major axis of the ampule with respect to the gravity vector and the magnitude of an applied magnetic field. Both transverse and axial fields will be used. A numerical model of the process is being developed to help in the understanding of the results and to guide parameter selection.

Progress to Date: Samples have been cast in a vertical attitude with a transverse magnetic field and without a field. Additional samples will be cast in both the vertical and other attitudes with both transverse and axial applied magnetic fields. Microstructural, electrical, and optical characterization methods will be applied to ascertain any differences in the relevant properties due to reduced convection. A 5T superconducting magnet has been installed (with funds from another project) and will be used to cast samples in an axial magnetic field. The numerical modelling work is continuing at ORNL.

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Vapor Crystal Growth of Electrooptical Materials

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Objectives: The goal of this project is to establish the effects of the processing environment, including gravitational orientation, on the nature and distribution of defects on materials of substantial technological interest that can be grown by the physical vapor transport method. The primary candidate materials are CdS CdTe.

Research Task Description: The investigation is intended to define a flight experiment that will take full advantage of the vapor crystal growth furnace being developed by Boeing Aerospace Company. That furnace has been made available to MSFC for one or more flights. The strategy includes the development of a 1-g crystal growth data base, coding of a numerical model of the growth process, and extensive characterization of both the starting materials and the grown crystals. A method to simulate reduced gravity has not been devised for this growth method but crystals will be grown at several orientations with respect to the gravity vector to assess the effects of gravity to the greatest extent possible on Earth. The material for the first flight, currently planned for mid-1992, will be CdTe.

Progress to Date: Favorable growth parameters in a laboratory furnace have been established. Work with Boeing was begun including work in the Boeing laboratory furnace in Seattle. Characterization of the starting materials as related to impurities and stoichiometry was initiated at UAH. Development of the numerical model has been delayed due to the reduction in funds for this project.

In addition to CdTe and CdS, high quality crystals of ZnTe, PbS, and PbSe have been grown using the technique developed under this project. The ZnTe crystals grown under this project have optical transmission and photoluminescence spectra that are featureless as opposed to various bands observed in the spectra of ZnTe grown by the travelling heater method (THM).

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Solution Crystal Growth of Organic and Polymetric Materials for Nonlinear Optics Applications

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Objectives: The major objective of the research is a thorough ground-based investigation of the basic aspects of solution growth of several representative diacetylenes and other organic compounds with nonlinear optical properties. Among the aspects to be studied are the influence of solvents, thermal gradients, concentration gradients, and, foremost, the influence of convective flows on the growth process and perfection of the crystal. Further problems to be studied are the evaluation of the influence of interface effects on defect incorporation into the crystals. Size and shape and growth habit of the crystal may play important roles in the growth process.

The results of the study will be used to determine the advantages of growing such crystals in space under a reduced gravity environment. Furthermore, these findings will be useful in solving current problems in the crystal growth of organic or biorganic substances with nonlinear optical properties.

Research Task Description: In this ground-based crystal growth experiment the plan of attack is the control of convection in a predictable manner as to be able to measure its effects and extrapolate to microgravity environment.

The following basic steps will form the bulk of the research task.

A small scale growth experiment will be carried out using the evaporatin method to produce crystals for further study and seeding. The bulk of the work will be performed using the controlled cooling method to produce the necessary supersaturation and induce nucleation and growth. Both seeded and unseeded runs will be introduced into this growth method to determine its effect on the growth habit. Reduction of convection will also be tried by the use of more viscous media such as gels, where the process is quasidiffusion controlled. The geometry of the growth cell and the position of the seed in this cell will be used as a major means in reducing convection effects.

Detailed characterization of the crystals will be performed to determine the densities of chemical and physical impurities. Such characterizations will be performed mainly by spectroscopic means as well as microscopy and x-ray diffraction and topography. These data will be correlated to the various growth parameters and methods in order to determine the influence of such parameters on the quality and size of crystals. Some simple modeling of the growth process will be attempted to acquire a better understanding of the kinetics and mechanisms involved.

Progress to Date: The apparatus and method have been set up for the preparation of a urethane substituted diacetylene ($R-C \equiv C-C \equiv C-R$), TCDU, not available in commerce.

The conditions (solvents, temperature, saturation, etc.) have been investigated for the growth of unseeded and seeded crystals of TCDU by the evaporation method. Single crystals of TCDU, in the form of plates of good optical quality have been grown from ethyl acetate-ethanol mixtures at room temperatures.

Work has been initiated to study the crystal growth of L-arginine phosphate (LAP), a very promising material for NLO applications. The dependence of its solubility on temperature and pH in aqueous solutions has been determined. Saturation and speed of evaporation have been studied. Seeded growth experiments in various configurations have been performed. The results of this work so far have allowed us to grow single crystals of LAP of extremely good optical quality for further experimentation.

The apparatus for the application of controlled and programmable cooling has been set up and the cooling regimes have been determined. Temperature stability of 0.1°C has been attained. Growth trials using this method have started. The results of several trials on LAP crystals using qualitative microscopic observations of surface roughness and growth step size show that the geometric position of the seed and the rate of saturation are two of the main contributors to crystal quality. These factors will now be quantified. This growth method, apparatus and growth parameters will lead eventually to a possible flight experiment.

Growth and Characterization of Doped GaSb_xAs_{1-x} with Current Induced Growth Interface Demarcation

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Professor August F. Witt

Research during the past funding period was directed at:

(a) *Growth Control in Bridgman and Gradient Freeze Geometries*

It was found that non-quantifiable deviations of the microscopic growth rate from the charge displacement rate are significantly reduced but not eliminated in heat-pipe based geometry with conventional temperature control. In customary control circuits of control T/C's at the high and low temperature reservoirs, the power input is fixed so as to achieve constant temperature at the reservoirs. Unavoidable changes in heat transfer characteristics associated with growth must thus result in a growth interface relocation, i.e. in a change of the microscopic rate of growth. The major deficiency of crystal growth by the Bridgman and gradient freeze techniques is found to be eliminated and the microscopic growth rate actively controllable when placing the temperature control sensors into the furnace cavity at appropriate positions relative to the desired crystal/melt interface location. In this control configuration all changes in thermal characteristics of the system will be compensated by power input changes, and the growth interface location as well as the axial thermal gradient will remain constant.

(b) *Quantitative Microscopic Growth Characterization*

Exploration of the potential of reduced gravity environment for growth research involving semiconductors has so far been seriously impeded by the nonavailability of sensitive, quantitative microscale characterization techniques. This deficiency has now been overcome with the development in this laboratory of NIR bright and dark field transmission microscopy of computational image analysis. Semiconductors with energy bandgaps larger than 0.7 eV can now be quantitatively analyzed for residual stress, free charge carrier density, precipitation and dislocation density with a spatial resolution of close to 1 μm . These analytical capabilities will enhance our ability to ascertain the conditions prevailing during crystal growth in a reduced gravity environment.

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2. SOLIDIFICATION OF METALS, ALLOYS, AND COMPOSITES

Immiscible Phase Incorporation During Directional Solidification of Hypermonotectics

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Objectives: The overall objective of this research is to develop a scientific understanding of solidification processes in immiscible (hypermonotectic) systems. The program is designed to provide an in-depth analysis of the manner in which the hypermonotectic phase is incorporated into the directionally solidified microstructure of immiscible alloys. Proposed applications, which include superconductors and high coercivity magnets, favor the use of aligned fibrous composite structures with a relatively high volume fraction of the fibrous immiscible phase. Fibrous composite structures can be produced in alloys of monotectic composition which do not exhibit liquid immiscibility. However, the composition of the monotectic in most systems limits the volume fraction of the fibrous phase to less than 10%. As a result, there is interest in solidifying off-monotectic (hypermonotectic) alloys in order to increase the volume fraction of the immiscible phase.

Production of the desired microstructures should be possible through directional solidifications of hypermonotectic alloys. However, several factors make processing difficult. One of the major barriers to producing high volume fraction aligned microstructures is settling of the denser immiscible phase during cooling. Analysis also indicates that density difference established in the melt during directional solidification may make cooperative growth of a fibrous structure in a hypermonotectic alloy very difficult under one-g conditions due to convection.

Research Task Description: The current research is focused on investigating morphological developments during directional solidification of transparent analog hypermonotectic alloys. This is being accomplished by directionally solidifying transparent hypermonotectic samples using a temperature gradient stage assembly fitted to an optical microscope. This approach permits direct observation of the incorporation of the immiscible phase at the growth front. The study encompasses both transparent monotectic systems that produce an irregular microstructure (low dome-height systems) and monotectic systems that produce aligned composite-like microstructures (high dome-height systems). In addition to binary systems, transparent ternaries will be utilized in which the miscibility gap height can be varied in order to bring about a transition in morphology from an irregular to an aligned composite-like structure. Results will be compared with those obtained from recent research on metallic hypermonotectic Cu-Pb-Al alloys of various dome heights that were processed aboard NASA's KC-135 zero-g aircraft.

The processing conditions utilize thin cells oriented horizontally in order to simulate low-g conditions and minimize sedimentation and convection. Various coatings have been utilized in order to prevent preferential wetting of the cell walls by the hypermonotectic liquid. The influence of growth rate, alloy composition, and thermal gradient on the incorporation of the immiscible phase into the structure is being examined.

Progress to Date: A temperature gradient stage assembly which permits direct observation of the solidification interface during directional solidification has been constructed, tested, and utilized to investigate hypermonotectic alloys. To date, work has been concentrated primarily on the succinonitrile-glycerol monotectic system in an effort to examine the mechanisms of incorporation of the immiscible phase at the growth front during directional solidification.

Fibrous aligned structures have been produced in hypermonotectic alloys up to two percent off of monotectic composition (9.5% glycerol as opposed to the monotectic composition of 7.5%). This was accomplished utilizing a steep thermal gradient and low growth velocity in an attempt to promote interfacial stability at the growth front and permit a cooperative growth process similar to that observed in eutectic systems. Changes in growth conditions to a higher growth rate result in the formation of rows of droplets oriented both parallel and perpendicular to the growth direction. Any further increase in growth rate leads to the formation of droplets of the immiscible phase in advance of the solidification front and the formation of a completely dispersed, non-directional microstructure.

These morphological transitions are similar to those that have been discussed by other investigators for alloys of monotectic composition. However, one notable difference is that the morphological transitions occurred at growth rates approximately one order of magnitude lower than those previously seen. This difference can be explained through an interfacial stability analysis. Testing on alloys in other transparent monotectic systems is planned.

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Containerless Processing of Refractory Metals and Alloys

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Objectives: Research is being conducted on the containerless processing of refractory metals and alloys. There are three primary objectives of the work. One is to understand the kinetics of solid phase nucleation from refractory containerless melts. The second is to determine the growth velocity of the solid phase as a function of deep undercooling in refractory melts. The third is to relate the microstructure to the degree of undercooling and solidification velocity in refractory melts.

Research Task Description: The first of the research objectives involves both maximum undercooling measurements and nucleation frequency determination. Maximum undercooling simply requires conducting a set of experiments on a number of samples under the best possible conditions to obtain the highest possible undercooling. The effort on nucleation frequency requires repeated experiments on given samples to evaluate the distribution of nucleation temperatures as a function of cooling rate. The second objective involves monitoring the rate of recalescence in the samples and extracting the solidification velocity from that data. The solidification velocity is related to the degree of undercooling. The third objective is accomplished by postprocessing analysis on specimens for types, sizes, amounts, distribution and morphology of resulting phases. This includes detailing the distribution of elements and therefore characterizing segregation. A number of techniques for microstructural analysis are used including x-ray diffraction, optical microscopy, scanning electron microscopy with energy dispersive analysis, microprobe and analytical transmission electron microscopy.

Experiments are being performed in the 100 Meter Drop Tube at the Marshall Space Flight Center. Usually the specimens solidify in free fall but occasionally conditions are adjusted to allow splatting with appreciable undercooling at the bottom of the tube. In addition, experiments using levitation melting are being conducted "on the bench" in the laboratory. These experiments employ solidification either with undercooling in the coil or with combinations of undercooling and rapid heat removal by splat quenching between pistons.

Progress to Date: Studies on the undercooling of Ti-Al alloys in the coil have been accomplished. For a given bulk undercooling, the solidification velocity of the beta phase was found to be faster than that of the alpha phase which was in turn faster than the solidification velocity of the gamma phase. In addition, the dependence of the solidification velocity of the gamma phase on undercooling exhibited two regimes. The rate of change of the solidification velocity was much greater above an undercooling of 100K. This difference in solidification kinetics is presently being investigated. A difference in solidification pathway observed was formation of metastable beta in sufficiently bulk undercooled samples within composition ranges where the alpha phase is the equilibrium primary phase expected. For this case, the metastable extension was determined.

Through a collaboration with Intersonics, Inc., liquid emissivities were measured as a function of temperature and composition in the Ti-Al system. Measurements were made in overheated and undercooled conditions. Using recalescence temperatures at small undercoolings and the measured emissivities enabled an accurate determination of the liquidus boundary in the 40-65 at.% Al region of the Ti-Al phase diagram.

The role of deep undercooling prior to rapid heat removal by splatting was modeled using parameters appropriate to the niobiumgermanium system. A one-dimensional finite difference model of transient heat flow characterized the moving interface conditions in terms of temperature, thermal gradient, velocity and composition. The numerical solution indicated diffusion controlled solidification at the quench wall commenced with liquid bulk undercooling and initial interface velocity of approximately 440K and 175 cm/s respectively, and at the conclusion of the splatting process, the interface undercooling were approximately 10K and 20 cm/s respectively. It is shown that prior undercooling certainly increases the volume fraction of rapidly solidified material but does not significantly affect the nucleation temperature. The decreasing effectiveness of the substrate with increases of overheat is manifested not only by significantly larger amounts of heat transferred to the substrate prior to nucleation, but also by lower cooling rates at the chill surface at nucleation.

A statistical approach has been undertaken in the study of nucleation. In the process over 400 experiments have been done on niobium in the drop tube. This data shows that the nucleation frequency, as depicted by a histogram of the number of nucleation events within given temperature intervals, is not clearly revealed until about 200 data points are obtained. The complete data set shows that the most probable nucleation temperature for niobium in the MSFC drop tube is 420K (about 15% of the equilibrium freezing point); the maximum nucleation temperature is 430K; and the minimum nucleation temperature is 400K. The histogram has a half width of 12K and can be fit by a Poisson distribution. The data is undergoing further analysis to be used for comparison to a variety of containerless processes.

A technique has been developed to measure the solidification velocity of the drop tube samples as they solidify during their free fall. Measurements on more than 230 of the niobium samples from the data set discussed above give a solidification velocity of about 18 m/s for the undercooling of about 15%. Comparisons are being made to theory.

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Dynamic Thermophysical Measurements in Microgravity

National Institute of Standards and Technology
Dr. Ared Cezairliyan
W-17, 428 (NASA Contact: R. Crouch, NASA HQ)
October 1, 1989 - September 30, 1990

Objectives: The main objective of this research is to develop accurate millisecond-resolution dynamic techniques which, in a microgravity environment, will enable the performance of thermophysical measurements on high-melting-point electrically-conducting solids and liquids at temperatures above 1500 K. The techniques when completed will enable, for the first time, the extension of accurate thermophysical measurements to temperatures above the limit (melting point) of the highly successful ground-based millisecond-resolution pulse-heating experiments. Thermophysical properties of interest include heat of fusion, heat capacity, electrical resistivity, thermal conductivity, surface tension, hemispherical total and normal spectral emissivities.

In addition to contributing to the advancement of general high-temperature science and technologies, the research is aimed at NASA flight support, specifically in the area of containerless processing. Our facilities (existing and under development) constitute a unique national capability in providing critically needed data on advanced high temperature materials under both equilibrium and nonequilibrium conditions. The research also has a strong component of shared technologies with other NASA supported programs in the areas of specimen heating, energy measurements, temperature mapping, and various other sophisticated measurement problems.

Research Task Description: A system, employing a millisecond-resolution dynamic heating technique, will be developed for measuring selected thermophysical properties at high temperatures in a microgravity environment. The technique is based on resistively heating the specimen up to its melting point and above in about one second by passing a large current pulse through it, and simultaneously measuring the experimental quantities with millisecond resolution.

The initial phase of this research requires the establishment of criteria for stability of the specimen when heated rapidly to temperatures above its melting point in a microgravity environment. For this purpose, a test package, which permits rapid heating of specimens in various geometrical forms (solid rod, tubular, triaxial, etc.), has been designed and constructed, and tested during microgravity simulations with NASA's KC-135 aircraft. A theoretical study of the stability of a current-carrying liquid has been conducted in conjunction with the experimental work to optimize the specimen geometry and operating conditions of the measurement system.

The second phase of this work involves applying the technique to definitive measurements of selected thermophysical properties of one or more representative refractory metals (such as, niobium, tungsten, etc.) at and above their melting points. In order to accomplish this, additional capabilities must be added to the measurement system to enable rapid and accurate measurements of the specimen temperature, temperature gradients in the specimen, and electrical power imparted to the specimen. The temperature measurements will be performed with two new high-speed pyrometers, a multiwavelength pyrometer (already developed) and a linear spatial scanning pyrometer (development nearly completed). The development of instrumentation for measuring imparted power is also underway.

In support of the above as well as of other NASA projects in the area of containerless processing, parameters relevant to temperature (pyrometric) measurements will be studied. These include optical

properties (such as normal spectral emissivity, reflectivity) of materials, assessment of the operation of new high-speed pyrometers, establishment of new easily-realizable temperature reference points, etc.

The overall system design will take into consideration the potential use of the system for other measurements and applications. Examples are: measurements of other thermophysical and related properties, measurements on other classes of substances, such as intermetallic compounds, investigations related to rapid solidification and supercooling, studies related to nucleation and kinetics of crystal growth, production and processing of pure materials, specialized fabrications, etc.

Progress to Date: A novel technique for measuring surface tension of liquid metals at high temperatures in a microgravity environment has been demonstrated. The specimen geometry involves a tubular specimen mounted in a triaxial configuration in which a fraction of the heating current is returned along the tube axis. Adjustments to the current enable a balance between magnetic and surface tension forces acting on the molten specimen. Rapid melting experiments, performed with the test package during microgravity simulations by NASA's KC-135 aircraft, have yielded a value for the surface tension of copper at its melting point which is in good agreement with literature data. Preliminary microgravity experiments have also been performed on tantalum specimens in order to provide baseline data for future definitive measurements of the surface tension of high-melting-point refractory metals for which there is a paucity of data.

An analytical study of the effect of vibrations on the stability of liquid tubular specimens has been carried out for the triaxial configuration. It was found that axisymmetric vibrations in which the inner and outer surfaces of the tube move in phase are always stable and that the out-of-phase modes become stable when the force balance among the magnetic and surface tension forces also includes a difference in gas pressure at the inner and outer surfaces. Plans are underway to redesign the experiment chambers so that a gas pressure difference can be maintained between the inside and outside of the specimen tubes during rapid melting experiments.

The design of a new automated modular measurement system has been completed. The measurement system includes: a computer-based data acquisition and control module (CDACM), a high-speed camera module, an experiment chamber module, and a high-current power module. The CDACM has been assembled and ground-based testing is underway. When construction and testing of the other modules is complete, the new measurement system will provide the capability of automated in-flight diagnostics and data analysis, thereby making more efficient use of KC-135 flight time than is presently possible with the existing test package. In addition, the modular design will provide greater flexibility in optimizing different requirements for measuring specific thermophysical properties of molten substances at high temperatures.

The high-speed multiwavelength pyrometer (constructed and tested earlier) has been used to measure the radiance temperatures at six wavelengths (in the range 522 - 906 nm) of niobium at its melting point. These ground-based measurements, repeated on several strip specimens, yielded highly reproducible results for the melting-point radiance temperatures, to within about 1 degree kelvin. Because of the simplicity and ease of performing pulse experiments on metal strips, it is believed that radiance temperatures at the melting point of selected metals are likely to form the necessary foundation for temperature reference points which can be easily realized for rapid secondary calibrations of optical pyrometers. This is particularly attractive in environments where lengthy primary calibration procedures are either undesirable or not possible such as microgravity research at high-temperatures involving flight experiments.

The literature data on normal spectral emissivity of selected high-temperature metals at their melting point has been reviewed. This study was motivated by recent results published by a major laboratory which show a common wavelength-independent behavior of the emissivity of several high-

temperature metals at their melting point. Our study of the emissivity data in the literature (including accurate values based on our radiance-temperature measurements on niobium) concludes that the normal spectral emissivity of high-temperature metals at their melting point is not constant but decreases with increasing wavelength in the range 400 - 1000 nm. Accurate knowledge of the wavelength dependence of spectral emissivity is important in the measurement of temperature of liquids and melts at high temperatures.

Automation, involving a computer-controlled incremental translation device and data acquisition, of the high-speed linear scanning pyrometer has been completed. This pyrometer, the only one of its kind, can measure spectral radiance temperature at about 1000 points along a straight line (25 mm long) on the specimen, with a complete cycle of measurements in about 1 ms. This pyrometer will be used to measure temperature gradients in a rapidly heating specimen providing data for diagnostic purposes and for determination of thermal conductivity, which will be a novel approach suitable for measurements at very high temperatures. Development of a procedure for the automatic calibration of the pyrometer has begun.

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Theory of Solidification

NASA Lewis Research Center
Professor Stephen H. Davis
NAG3-747
October 14, 1986 - October 9, 1992

Objectives: The research concerns the effort to understand on a quantitative level how various factors affect the morphology of a solidification front of binary materials. These factors include buoyancy-driven convection with and without Soret diffusion, forced flow, phase-change convection, crystal and kinetic anisotropies and effects of bounding surfaces. The central theme is the understanding of the phenomena through the study of the instability behavior of the appropriate coupled systems.

Research Task Definition: The research entails the study of coupled systems using analytical methods, with the aim of identifying new mechanisms of behavior and new physical effects.

Progress to date: In the past year we have concentrated on two aspects. On the one hand we have considered rapid solidification under conditions that the interface is governed by non-equilibrium thermodynamics. A self-consistent model is used and the morphological instability problem is reexamined. A new pulsatile mode of instability is uncovered which may help explain the appearance of banded structures. The nonlinear behavior of this mode have been examined as well.

On the other hand we have examined Soret convection linked to a solid-liquid front. Both theory and experiment show how the coupling yield alterations of the interface morphologies.

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Metals and Alloys

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In-House

There are three general categories of experiments in this area, those aimed at understanding the influence of undercooling on nucleation and on macro and microsegregation in bulk samples, those directed at fundamental understanding of dendritic and cellular growth in directional solidification, and those in support of a proposed Space Shuttle experiment on macrosegregation in metallic alloys.

Experiments on bulk undercooling have led to an increased appreciation of the role of surface tension in heterogeneous nucleation. In the Pb-Sn system one primary phase, Sn is an effective nucleant for Pb, but Pb is not an effective nucleant for Sn. Based on traditional considerations of lattice matching the nucleation behavior would be expected to be reciprocal. Instead, because of differences, in interfacial energies, nonreciprocal nucleation is observed. Contrary to expectation, macrosegregation was found to increase in this system with increasing undercooling. The macrosegregation was strongly influenced by melt off and settling of lead dendrites in the less dense alloy liquid.

Experiments designed to test our ability to differentiate among theories describing cellular or dendritic growth have been performed using PbAu and PbSn alloys. Directional solidification was conducted with the hot end above the cold for thermal stability. The PbAu alloys also offered solutal stability. In the slow growth regime where predictions of the theories differ most, convection still interfered with microstructural development. (Only if the solute rich liquid were equal in density to the original liquid for all compositions and temperatures could success be expected for ground based studies.) In keeping with the findings of the ground based work, a flight experiment was proposed for performance in the AGHF. Additional studies have indicated that prior work reported in the literature suffers from various effects of convection frequently not acknowledged by the investigators.

Other experiments designed to improve understanding of solidification of alloys used superalloys cast on the KC-135 aircraft. With commercial alloys chosen by Pratt and Whitney, it has been shown that the solute rejection behavior of multicomponent alloys can, to a first order, be described as a sum of binary alloy results, ie the binary alloy phase diagrams predict the behavior of at least some multi-component alloys. The partition coefficients appeared to be constant over a wide range of composition. And the temperature for the final portion of solidification was approximately constant, simplifying analysis of the experimental work. The superalloys showed macrosegregation which could be explained by the directional solidification model of Bower, Brody, and Flemings. Dr. Tewari and co-authors Curreri and Lee of Marshall have four papers in print or submitted for publication describing this work. A major finding is that for aligned single crystal alloys the primary dendrite spacing does not change as the KC-135 executes variable acceleration maneuvers.

Publications

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Fluid Flow in Partly Solidified Systems

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NAG3-560 (NASA Contact: T. Glasgow, LeRC)
December 1989 - December 1990

Objectives: The objective of the research is to identify the conditions under which channel segregation occurs during the solidification of alloys over a freezing range, and to make comparisons between materials having different physical properties, summarized by the Lewis and Prandtl numbers.

Research Task Description: During solidification of materials which freeze with a dendritic morphology and develop a mushy zone, thermo-solutal convection can develop in the form of solute plumes above an advancing growth front, with concomitant segregation channels forming below the plumes within the dendritic array. The object of the research is to ascertain how these channel plumes originate and what controls their dimensions and flow rates. In particular, it is of interest to demonstrate the generic nature of the phenomenon in materials having different Prandtl numbers, thus allowing the development of a common analysis to justify extrapolation from transparent systems with higher Prandtl numbers to opaque metallic systems with lower numbers.

Progress to Date: Experimental observations and measurements have been largely completed, as far as is possible, with lead base alloys ($Pr \gtrsim 10^{-2}$), aqueous ammonium chloride ($Pr \approx 6$) and succinonitrile-ethanol ($Pr \approx 30$) and are continuing with molten ionic salts ($Pr \gtrsim 10^{-1}$), to complete the picture. In the transparent materials the measured data include plume flow velocities, effective widths and spacings, plume compositions and temperatures. It is found that these fit a modified Poiseuille type model for streamline flow: velocities are slightly in excess of those which would be required to establish complete thermal equilibrium, but far below those leading to turbulence. In the aqueous system, high resolution video-recording of dendrite particle movements has allowed precise characterization of plume velocity profiles and confirmation of the model.

Publications

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Containerless Processing of Oxide Superconductors

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Dr. Robert Bayuzick
Dr. Richard Hopkins, Westinghouse R&D Center

Objectives: Because of the high reactivity of oxide superconductors, they are an excellent candidate for containerless processing experiments. Benefits are expected from melt processing and undercooling of these materials that cannot be realized by conventional ceramic bulk processing techniques. The $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ or 1:2:3 compound has been chosen as a prototype for these studies for two primary reasons; the phase relations are reasonably well known, and as a peritectic compound, the possibility of solidifying the 1:2:3 phase from an undercooled melt is reasonably high. The experimental objectives are to explore the melting, undercooling and solidification behavior of these materials in a containerless environment and to characterize the microstructural and superconducting properties of the resultant materials. Comparison of these melt processed materials with ceramic, melt textured, and directionally solidified materials will help to elucidate the advantages or disadvantages of containerless processing on oxide superconductors. The techniques developed as a result of this project will be applicable to oxide superconductors in general and will provide additional avenues for research in this field.

Research Task Description: High purity powders from 10-300 μm of the 1:2:3 compound will be prepared by Westinghouse and processed in a 2 meter drop tube at Vanderbilt University. This drop tube has been specially designed to allow processing in oxidizing atmospheres and to provide for the melting and solidification of oxide superconductors. Full characterization of the resultant materials by both Vanderbilt and Westinghouse will be accomplished.

Progress to Date: This project was initiated on July 1, 1990. As of this reporting date the drop tube is under construction and starting materials are being prepared.

Containerless Processing of Undercooled Melts

University of Wisconsin-Madison
Professor John H. Perepezko
Grant NAG-771 (M.B. Robinson MSFC)
October 1989 - October 1990

The main objective of the research project is to evaluate the undercooling and resultant solidification microstructures in containerless drop tube processing of the alloys as an experience base for microgravity experiments. The degree of liquid undercooling attainable in a laboratory scale (3m) drop tube can be altered through the variation of processing parameters such as melt superheat, droplet size and gas environment. In a given sample, the competitive nucleation and growth kinetics between equilibrium and metastable phases controls microstructural development. This solidification behavior is evaluated through metallography, thermal analysis and x-ray diffraction examination in conjunction with calorimetric measurements of falling droplet temperatures and a heat flow model of the processing conditions.

In the current program studies, solidification microstructures are being examined in selected Ni, Fe, and Mn based systems. The specific alloy selection is based on a metastable phase diagram analysis that allows for the identification of unique microstructures and microstructural transitions that may be produced by microgravity containerless processing. Based on this approach a duplex partitionless solidification reaction has been identified in several alloys near the eutectic composition in the Ni-V system. The reaction can be thought of as a limiting case of a eutectic process, $L \rightarrow \alpha + \beta$ in which α and β have the same composition as the liquid. Drop tube experiments are being used to understand and model the competitive kinetics controlling the duplex partitionless reaction. Near equiatomic Mn-Al alloys represent an important class of permanent magnet materials. The key ferromagnetic phase is a metastable structure produced by solid state heat treatments. Recent drop tube studies have demonstrated for the first time that the metastable ferromagnetic phase can be produced from the liquid provided high undercooling is achieved. A solidification processing kinetics model is being applied to optimize the yield of metastable phase. In the above studies a new calorimetric system is being used to measure the temperature of falling drops during containerless processing. In another study on drop tube processing of magnesium metasilicate liquids a novel glass-ceramic microstructure has been produced in samples that undercool into a liquid phase miscibility gap before the onset of crystallization.

Publications

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Presentations

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Thermosolutal Convection and Macrosegregation in Dendritic Alloys

University of Arizona
Professor D. R. Poirier
Professor J. C. Heinrich
NAG 3-1060 (NASA Contact: T. K. Glasgow, LeRC)
July 18, 1989 - October 17, 1991

Objectives: The major objective of the program is to develop a computer model for studying thermosolutal convection and associated macrosegregation phenomena in dendritically solidifying alloys.

Research Task Description: Comparison between the calculated macrosegregation and experimental results of other NASA-sponsored investigators will be made. A major feature of the code will be to simulate the nonlinear convection that leads to the formation of a macrosegregation defect, called freckles. The calculations will include the effects of varying solidification rate, thermal gradient, and composition in Pb-Sn and Pb-Sb alloys. Time permitting, comparisons between calculated and experimental results in solidified $\text{NH}_4\text{Cl-H}_2\text{O}$ solutions will also be made.

The effects of reducing the magnitude of gravitational acceleration and changing its direction on thermosolutal convection and the attendant macrosegregation, will be studied by using our finite element code for the fully nonlinear convection problem. The goal of these calculations will be to assist experimentalists in planning work in the low-gravity environment.

Progress to Date: The finite element code (used for grant NAG3-723) has been modified so that it can be used to simulate unsteady dendritic solidification in a vertical mold. An important feature of the code is that it calculates the adjustment of the volume fraction of the interdendritic liquid, as convection occurs in the mushy zone. Calculations have been done for a Pb-Sn alloy which show the development of freckles during directional solidification--the first of their kind. In addition, pockets of segregated liquid form within the mushy zone, itself, and the all-liquid zone selectively penetrates into the mushy zone producing additional segregation zones.

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Containerless Studies of Nucleation and Undercooling

Jet Propulsion Laboratory
Dr. Eugene H. Trinh
January 1989-January 1990

Objectives: The long term research objectives are experimental and theoretical studies to determine the achievable limits of undercooling using acoustic and other means of sample levitation and manipulation, to study the characteristics of heterogeneous nucleation using levitated materials in 1 G and in microgravity, to measure the physical properties of significantly undercooled melts, and to determine the characteristics of solidification under conditions allowed by both containerless processing and low gravity.

Research Task Description: Ground-based experiments and investigations aboard the NASA KC-135 aircraft are carried out to levitate, melt, undercool, and solidify 0.5 to 3 mm specimens of low-melting pure metals and alloys (Ga, In, Sn, Al, Al-Cu alloys), as well as inorganic compounds (O-Terphenyl, Succinonitrile), and low melting glasses. Non-perturbing measurement techniques for the measurement of the density, surface tension, viscosity, refraction index, sound velocity, specific heat, and thermal diffusivity are being refined and developed to probe the physical state of levitated undercooled melts. The quantitative evaluation of the effects of external physical stimuli on the nucleation onset is also being carried out to rigorously document the advantages of experimentation in microgravity. In addition to the undercooled liquid phase, the solidification process under containerless conditions has also been investigated for model materials in 1 g. Closer examination of the thermal and flow environment within and outside the melt is being carried out experimentally and theoretically. Current experimental approaches involve the utilization of controlled environment ultrasonic and electromagnetic levitators and noncontact probing techniques.

Progress to Date: 1 g undercooling of a wide variety of materials has demonstrated that the containerless environment indeed enhances the ability to access the metastable state. On the other hand, definite evidence for secondary influence of the levitation mechanisms implemented on the ground has been obtained. The undercooling and dendritic solidification of levitated succinonitrile has been carried out, and preliminary measurement of the dendritic growth velocity on the surface of a spheroidal droplet has been obtained. Experimental evidence of ultrasonically-induced nucleation of undercooled succinonitrile has been obtained, together with the capability for hypercooling. Preliminary data for the enthalpy of undercooled pure aluminum in an electromagnetic levitator have been gathered.

Publications

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Ostwald Ripening of Solid-Liquid Mixtures

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Dr. S. C. Hardy, NIST
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Objectives: The objective of this program is to use the unique conditions provided by spaceflight to study the kinetics of Ostwald ripening. The data derived from this experimental work will provide baseline data for the field and thus permit the refinement of existing theories of the kinetics of first-order phase transformations. In addition, as the Ostwald ripening process has a major impact on the properties of materials, the experimental results will yield information which can be used to improve the properties of materials containing dispersed phases, such as precipitation hardened alloys.

Research Task Description: A particularly ideal system to use in these experiments is a two-phase mixture consisting of solid particles in a liquid. Since the coarsening rate of the solid particles in such a system is comparatively fast, and in a properly chosen system the particles can be spherical, the experiments can serve as a careful test of theory. However, experiments performed in systems with a low volume fraction of solid particles, where the theory is most accurate, under terrestrial conditions shows that buoyancy driven convection of the solid particles is prevalent and thus the experiments do not satisfy the theoretical requirements of fixed spatial locations of the particles. To eliminate this problem, it is necessary to perform the experiments in the reduced gravity environment of space.

Progress to Date: During the year, we have:

- (1) Measured the kinetics of the development of grain boundary grooves in the Pb-Sn system. Using these measurements the combination of the interfacial energy and diffusion coefficient used to compare the theoretically predicted and experimentally measured coarsening rate constants was determined. Thus, these experiments provide a check on these difficult to measure thermophysical parameters which have been determined by other workers. It was found that the thermophysical parameters used previously to compare the theoretically predicted coarsening rates in Pb-Sn and the experimental measurements are consistent with those found from the grain boundary grooving experiment. Thus, the source of the disagreement between theory and experiment remains unidentified.
- (2) Continued our theoretical work on the effects of convection on Ostwald ripening. We found that in the limit when $P \ll 1$, where $Pe = UR/D$, U is the velocity of the particle with respect to the fluid, R is the particle radius, and D is the solute diffusion coefficient, and the particles move at a constant velocity or, according to Stokes law, the dynamics of the coarsening process in the solid-liquid system are not describable in terms of simple temporal power laws. Thus, the system does not coarsen in a self-similar fashion.
- (3) We have been developing a numerical procedure for calculating the time-dependent change in the shape of an arbitrary particle radius distribution during the initial stages of Ostwald ripening. We are interested in the dynamics of the approach of the system to the longtime attractor states such as those determined by Lifshitz and Slyozov and others. We are using a method of lines technique to solve the nonlinear integro-differential equation describing the temporal evolution of the particle radius distribution function.

Publications

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Influence of Convection on Microstructure

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Jayshree Seth
Aditya Mohanty
NAG8-753 (NASA Contact: F. Szofran, MFSC)
August 1988 - August 1991

Objective: To gain an understanding of the influence of microgravity on the microstructure of eutectics especially MnBi-Bi.

Research Task Descriptions:

1. Via theoretical calculations determine the influence of convection on the microstructure of fibrous eutectics.
2. Via theoretical calculations determine the influence of the Soret effect (thermal diffusion) on eutectic microstructure.
3. Estimate the Soret coefficient of eutectic MnBi-Bi melts using laboratory data and data from the flight experiment of Dr. David Larson at Grumman.
4. Via theoretical calculations determine the influence of convection on eutectic microstructure when one phase projects out into the melt ahead of the other phase.
5. Experimentally determine the influence of vibration during solidification on eutectic microstructure.
6. Experimentally determine the influence of centrifugation during solidification on eutectic microstructure.

Progress to Date: Tasks 1, 2, 4 and 5 above have been completed. Convection is predicted to coarsen eutectic microstructure more when the structure is rod-like rather than lamellar, and more when one phase projects out than for a planar interface. However, the effect is still not large enough to explain the experiments of Larson and Pirich that showed a two-fold decrease of MnBi rod spacing when solidification was carried out in space or with a magnetic field applied.

Results show that the Soret effect can either decrease or increase the inter-phase distances in eutectic solidification, depending on the sign of the Soret coefficient. Again, it does not seem likely that this effect is large enough to explain the Larson/Pirich results.

Ground-based experiments designed to yield values of the Soret coefficient for Mn-Bi eutectic were interesting but inconclusive. The eutectic was placed in capillary tubes and held vertically in a furnace with the temperature increasing with height. A rapid separation occurred. This separation was attributed to settling of the slow-melting phase during heatup. After many days, steady state concentration profiles were obtained that suggest the presence of very gentle buoyancy-driven convection. Flight experiments should be designed aimed specifically at measuring the Soret coefficient, because buoyancy-driven convection appears to be impossible to completely avoid on earth.

Vibration during solidification of lead-tin eutectic produced a large increase in the interlamellar spacing. This increase is beyond that expected for the amount of convection produced. Our previous experiments with spin-up/spin-down (accelerated crucible rotation) did not change the lamellar spacing at

all. On the other hand, vibration gave no separation of lead and tin, while a significant separation was obtained with spin-up/spin-down. Spiralling was not observed with vibration.

We have prepared ampoules containing Mn-Bi eutectic for solidification in centrifuges in France, Canada, and the Soviet Union. Prior work on other systems has shown some surprising changes in microstructure and compositional homogeneity. Basically the centrifuge offers a means of altering the convection without perturbing the growth rate as spin up/spin-down and vibration do.

Publications

Seth, J., "The Effect of Convection on Lamellar Spacing of a Eutectic Growing with a Stepped Interface," M.S. Thesis, Clarkson University, 1990.

Mohanty, A.P., "Determination of the Soret Coefficient of Mn-Bi Melts," M.S. Thesis, Clarkson University, 1990.

Caram, R., Chandrasekhar, S., and Wilcox, W.R., "Influence of Convection on Rod Spacing of Eutectics," J. Cryst. Growth **106**, 294-302 (1990).

Caram, R. and Wilcox, W.R., "The Soret Effect in Eutectic Solidification," J. Cryst. Growth, 1990 (submitted).

Caram, R., Banan, M., and Wilcox, W.R., "Directional Solidification of Pb-Sn Eutectic with Axial Vibrations," J. Cryst. Growth, 1990 (submitted).

Presentations

Caram, R. and Wilcox, W.R., "Effects of Thermotransport during Eutectic Solidification," *Eighth American Conference on Crystal Growth*, Vail, Colorado, July 1990.

Caram, R. and Wilcox, W.R., "Numerical Modeling of Rod-like Eutectic Growth with Convection," *Eighth American Conference on Crystal Growth*, Vail, Colorado, July 1990.

Modelling Directional Solidification

Clarkson University

Dr. William R. Wilcox

M. Banan

J. Zhou

NAG8-831 (NASA Contact: F. Szofran, MSFC)

May 1, 1990 - April 30, 1993

Objective: To gain an improved understanding of the influence of gravity on the directional solidification of compound semiconductors and their alloys.

Research Task Description: This is a continuation of a previous NASA grant. The following two tasks have been undertaken under the current grant.

1. Determine experimentally the influence of current pulses and vibration on compositional homogeneity and microstructure of InSb-GaSb alloy.
2. Determine experimentally the variation of freezing rate during a spin-up/spin-down cycle by using current pulses.

Progress to Date: The variation of In/Ga with distance down the ingot corresponded to complete mixing in the melt, regardless of whether current pulses, vibration, or spin-up/spin-down was employed or not. This indicates that there was sufficient buoyancy-driven convection in this apparatus to completely mix the melt at the low freezing rates employed to avoid constitutional supercooling. The number of grain boundaries and twins was increased by application of current pulses, but decreased by vibration of the ampoule.

Doped InSb is being used with current interface demarcation to determine the microscopic variation of freezing rate. The technique have been successfully developed, but not yet used with spin-up/spin-down.

A technique was developed for measuring the heat transfer coefficient between the material in an ampoule and the furnace wall. This heat transfer coefficient has been used in many theoretical treatments of heat transfer in the directional solidification, but until now there was no means for measuring it.

Publications

M. F. Larrousse and W. R. Wilcox, "Interfacial Mass Transfer to a Cylinder Endwall during Spin-up/Spin-down," Chem. Eng. Sci. **45**, 1571-1581 (1990).

Neugebauer, G.T. and Wilcox, W.R., "Experimental Observation of the Influence of Furnace Temperature Profile on Convection and Segregation in the Vertical Bridgman Crystal Growth Technique," in *Proceedings of 41st Congress of the International Astronautical Federation*, 1990.

Banan, M., Gray, R.T., and Wilcox, W.R., "A Novel Approach to Determine the Heat Transfer Coefficient in Directional Solidification Furnaces," J. Cryst. Growth, 1990 (submitted).

Presentations

Wilcox, W.R., "Transport Phenomena in Directional Solidification," Tufts University, March 1990.

Banan, M., Gray, R., and Wilcox, W.R., "Directional Solidification of InGaSb," Gordon Research Conference on Crystal Growth, Ventura, March 1990.

Wilcox, W.R., "Influence of Low Gravity, Magnetic Field, Vibrations, Current Pulses and Accelerated Crucible Rotation on Directional Solidification of Indium Gallium Antimonide," LIMSI, Orsay, April 1990.

Banan, M., Gray, R.T., and Wilcox, W.R., "GaSb-InSb Alloy Growth," CSME, Toronto, June 1990.

Banan, M., Gray, R., and Wilcox, W.R., "Solidification and Characterization of Indium Gallium Antimonide," Northeast Regional Meeting of the American Chemical Society, Potsdam, NY, June 1990.

Banan, M. and Wilcox, W.R., "Effect of Axial Oscillation of the Growth Ampoule on Solidification of $\text{In}_x\text{Ga}_{1-x}\text{Sb}$," *Eighth American Conference on Crystal Growth*, Vail, Colorado, July 1990.

Wilcox, W.R., "Crystallization of $\text{In}_x\text{Ga}_{1-x}\text{Sb}$," Ioffe Physico-Technical Institute, Leningrad, August 1990.

3. FLUIDS, INTERFACES, AND TRANSPORT

Process Modelling for Materials Preparation Experiments

University of Alabama in Huntsville
Center for Microgravity and Materials Research
Dr. J. Iwan D. Alexander
Dr. Jalil Ouazzani
Dr. Franz Rosenberger
NAG8-790 (NASA Contact: Dr. S.L. Lehoczky, MSFC)
August 1989 - July 1992

Objectives: The objectives of this program are the exploitation and improvement of available numerical techniques in order to formulate and solve useful models of transport processes in (microgravity) materials preparation experiments. Recognizing the fact that the potential of the most sophisticated modelling techniques cannot be fully realized if the physical properties, boundary and operating conditions are not well characterized, we aim to develop a comprehensive research program which coordinates a study of these essential ingredients with the development of numerical models for two specific crystal growth systems: (1) growth of mercury cadmium telluride (MCT) from the melt by the Bridgman-Stockbarger technique and (2) growth of triglycine sulfate (TGS) from solution.

Research Task Description:

Transport property studies under representative crystal growth conditions (including undercooling and supersaturation):

Kinematic viscosity and solute diffusivities of molten mercury cadmium telluride as a function of temperature and composition.

Solute diffusivity in triglycine sulfate - water solutions.

Numerical modelling studies (using experimentally determined transport coefficients and boundary conditions):

The development of an algorithm which employs spectral techniques to solve a moving boundary problem. Subsequent incorporation of this technique into a pseudo-spectral collocation method that we have previously applied to convective-diffusive transport in melts. This will be followed by the development of numerical methods for the specific moving boundary problems associated with the growth of MCT by the Bridgman-Stockbarger technique.

Progress to Date:

The vapor pressure of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ in the compositional range of interest ($0 < x < 0.2$) lies between 15 and 40 atm. This, together with the relatively high melting temperatures involved, poses great difficulties for melt viscosity measurements with conventional techniques. Hence, we have developed a novel technique that is well suited to high pressure, high temperature conditions. The kinematic viscosity is obtained through gravimetric monitoring of the mass redistribution by melt flow in a capillary that connects two sealed quartz chambers. This technique is highly accurate, as revealed by tests with room temperature liquids and low melting point metals of known viscosity. Expansion of the instrumentation to high temperatures is in progress.

Recent work has shown that the diffusivities of saturated and supersaturated solutions can be drastically lower than in the corresponding undersaturated solutions typically used for diffusivity determinations. The measurement of diffusivities of supersaturated solutions in diaphragm cells, that tend to stimulate nucleation, is difficult. Hence, we are developing a technique that minimizes nucleation stimulation. Diffusivities are obtained through the interferometric monitoring of the evolution of the concentration profile between two initially sharply bound solutions of slightly different concentration. Though similar to the widely used Gouy technique, our approach allows for a simpler evaluation of the interferometric data.

As a first step in the simulation of the solution growth of TGS, we have developed a 2-D model, with concentration-independent diffusivity and idealized heat transfer conditions, for the system used on Spacelab 3. The results show that, for the conditions of this experiment, diffusion dominated transport can prevail if the residual acceleration remains at or below a steady $10^{-6}g$ level. The suppression of convection at somewhat higher acceleration levels would require other operating conditions, such as lower cooling rates. The sensitivity to periodic acceleration perturbations was found to be complex.

Considerable progress was also made toward the development of numerical codes for the MCT directional solidification problem. Employing a pseudo-spectral Chebyshev collocation technique, 3-D convection (without solidification) in a cylinder was treated. Steady and time-dependent moving boundary problems, involving heat conduction alone, have been solved, based on a 2-D Cartesian code developed earlier in our group. An axisymmetric (stream-function vorticity) code is currently being developed which will eventually be incorporated with the moving boundary code to solve solidification problems with melt convection.

Publications

Jin, W.-Q., Alexander, J.I.D. and Rosenberger, F., "Kinematic Viscosity Measurements at High Temperature and High Pressure - A Novel Technique, in preparation.

Nadarajah, A., Rosenberger, F. and Alexander, J.I.D., "Modelling the Solution Growth of TGS Crystals in Low Gravity," J. Cryst. Growth **104**, 218 (1990).

Rosenberger, F., Alexander, J.I.D., Nadarajah, A. and Ouazzani, J., "Influence of Residual Gravity on Crystal Growth Processes," Micro. Sci. Techn. **3**, 162 (1990).

Pulicani J.P. and Ouazzani, J., "A Fourier-Chebyshev Pseudospectral Method for Solving Steady 3-D Navier-Stokes and Heat Equations in Cylindrical Cavities," Computers and Fluids, in print.

Pulicani, J.P., Krukowski, S., Alexander, J.I.D., Ouazzani, J. and Rosenberger, F., "Convection in an Asymmetrically Heated Cylinder," Phys. Fluids, submitted.

Alexander, J.I.D., Amiroudine, S., Ouazzani, J. and Rosenberger, F., "Analysis of the Low-Gravity Tolerance of Bridgman-Stockbarger Crystal Growth. II. Transient and Periodic Accelerations," J. Cryst. Growth, submitted.

Rosenberger, F., "Boundary Layers in Crystal Growth, Facts and Fancy," in *Lectures on Crystal Growth* (H. Komatsu, ed.), in print.

Thermo-Diffuso Capillary Phenomena

NASA Lewis Research Center
Dr. R. Balasubramaniam
Dr. L. H. Dill
In-House

Objectives: The main objective of this program is to understand the motions of bubbles and droplets due to thermocapillary effects (Marangoni flow) in a reduced gravity environment.

Research Task Description: Analytical and numerical studies are being performed to predict the terminal and transient velocities of immiscible bubbles and droplets in a host fluid possessing a uniform temperature gradient. The terminal velocity of a bubble has been calculated including the effects of inertia and convection, i.e., for non-negligible values of the Reynolds and Marangoni numbers. The steady thermocapillary migration of a gas bubble in the presence of an insoluble surfactant is also being analyzed.

Experiments are also being conducted using an immiscible density matched liquid-liquid system to obtain migration data for droplets and also visualize the thermocapillary flow that is induced within the droplet.

Progress to Date: The research performed in this area has resulted in publications/presentations that are cited below. Analytic studies have been completed to predict (i) the terminal velocity and small deformations of a droplet for small Ma and arbitrary Re, (ii) the migration velocity of a large gas slug in a heated tube, (iii) the transient migration velocity and time taken to reach steady state for bubbles and droplets in creeping flow, (iv) numerical calculations of terminal velocities for a spherical bubble for Re and Ma up to a thousand. The finite difference code that was developed has been modified to account for surfactant effects. Preliminary results suggest that surfactants can substantially reduce thermocapillary migration rates. The unsteady thermocapillary migration of an isolated drop growing or shrinking due to mass transfer has been analyzed for both viscous flow and finite Reynolds number conditions. Migration data and flow visualization using particle tracking in a laser light sheet have been obtained for drops of vegetable oil, methanol and water-methanol mixtures in a silicone oil host liquid.

Publications

Balasubramaniam, R., and Lavery, J. E., "Numerical Simulation of Thermocapillary Bubble Migration for Large Reynolds and Marangoni Numbers," Num. Heat Transfer, Part A 16, 175-187 (1989).

Rashidnia, N., and Balasubramaniam, R., "Thermocapillary Migration of Liquid Droplets in a Temperature Gradient in a Density-Matched System," Experiments in Fluids, September, 1990 (accepted)..

Balasubramaniam, R., and Rashidnia, N., "Interfacial Tension Measurement of Immiscible Liquids Using a Capillary Tube," AIChE Journal, submitted.

Dill, L.H., "On the Thermocapillary Migration of a Growing Drop," J. of Colloid Interface Sci., submitted.

Presentations

Balasubramaniam, R., and Rashidnia, N., "A Comparative Flow Visualization Study of Thermocapillary Flow in Drops in Liquid-Liquid Systems," AIAA Paper No. 91-0311, *29th Aerospace Sciences Meeting*, Reno, Nevada, Jan 1991.

Balasubramaniam, R., and Dill, L. H., "Thermocapillary Bubble Migration - An Oseen-Like Analysis of the Energy Equation," *IUTAM Symposium on Microgravity Fluid Mechanics*, Bremen, West Germany, Sept 1991.

Fluid Mechanics and Mass Transfer in Melt Crystal Growth: Macro- and Micro-Scale Analysis of Controlled Solidification

Massachusetts Institute of Technology
Professor Robert A. Brown
NAS 7645 (NASA Contact: Mark Lee)
October 1, 1989 - September 31, 1992

Objectives: This program is aimed at fundamental understanding of the interactions of heat and mass transfer, melt flow and interface morphology in the design and interpretation of solidification experiments for growth of crystals on earth and in space. The ongoing research is a mixture of state-of-the-art computational studies of macroscale transport in large-scale crystal growth systems and of microscale formation of cellular solidification structures. An experimental program for studying mechanisms for microstructure formation in solidification and is support by theoretical and computational analysis of cellular and dendritic crystal growth of binary alloys.

Research Task Description: The research being performed under this program is divided into several distinct tasks according to the application of the research to the understanding of either macroscale or microscale features in solidification. These are:

Simulation of Directional Solidification. Application of transient and steady-state calculations of axisymmetric convection in directional solidification systems to analysis of both vertical gradient freeze and Bridgman-Stockbarger configurations for growth of semiconductor and oxide crystals. This project includes development of the simulators to include detailed models for radiative heat transfer and coupling between the temperature, solutal and convection fields.

Cellular and Dendritic Crystal Growth in Thin-film Solidification. Experimental and computational analysis of the dynamics of cellular interface formation in thin-film, two-dimensional directional solidification of a binary alloy. Development of a new numerical method for analysis of the transition from shallow to deep cellular surfaces is included.

Simulation of Small-Scale Floating Zones. Simulation of heat transfer, convection and interface morphologies in small-scale floating zones. Analysis should predict the onset of instabilities in the zone caused by both surface-tension-driven convection and by interactions of the zone shape with heat transfer.

Three-dimensional Convection in Solidification. The development of the first numerical method for analysis of flow and interface morphology with three-dimensional convection in directional solidification. This research involves the development of numerical algorithms for solving three-dimensional convection problems with solidification which are robust on medium-grain parallel processing computers.

Progress to Date: The progress to date in each of these projects is summarized here. Publications that describe these developments are listed below.

Simulation of Directional Solidification. The simulation for heat transfer, convection, dopant transport and interface morphology in directional solidification has been applied to the analysis of vertical Bridgman growth of HgCdTe and the gradient freeze system for growth of GaAs crystals. In both systems experimental observations of the melt/crystal interface morphology and of dopant segregation

are reproduced and design issues that impact dopant uniformity are addressed. The simulator has also been used to explore the usefulness of the concept of the effective segregation coefficient for axial segregation in directional solidification. Bounds for the accuracy of this concept have been established. The simulation for directional solidification has been extended to include a complete analysis of diffuse gray in the furnace; this extension makes possible design calculations that connect the furnace configuration with crystal quality through dopant segregation and defects in the crystal.

Cellular and Dendritic Crystal Growth in Thin-film Solidification. Progress in understanding cellular solidification has come in both theoretical and experimental parts of the program. First, calculations of the transition from shallow to deep solidification cells has demonstrated conclusively that there is no mechanism for selection of cells of a unique wavelength, based on the existence of steady-state solutions. Moreover, the first fully dynamical simulations of collections of cells have shown that multiple steady, time-periodic and apparently chaotic states are possible. Also, the apparent wavelength of the cells decreases very rapidly with increasing growth rate through a tip splitting mechanism that is connected with the codimension-two bifurcation between cell shapes with spatially resonant wavelengths. This dynamics is not captured by classical Eckhaus analysis for wavelength selection near the onset of cellular solidification. Experiments using succinonitrile-acetone alloys in our newly developed thin-film solidification system agree qualitatively with the theoretical predictions; chaotic dynamics are observed that involves a band of wavelengths which migrates to lower mean values as the growth rate is increased.

Simulation of Small-Scale Floating Zones. A complete simulation of axisymmetric convection, heat transfer and interface morphologies in small-scale floating zone systems has been developed for solidification of binary alloys. This simulation is being extended to the analysis of the stability of these steady-state flows to nonaxisymmetric disturbances to look for the onset of the traveling wave states caused by surface-tension-driven convection.

Three-dimensional Convection in Solidification. The finite-element/Newton method developed by this research group for solution of the coupled convection/solidification problems is being adapted for use on medium-grain parallel computers; our first calculations are on an Intel i860 hypercube with 32 vector computational elements. Initial development work has focussed on the development of direct methods for LU decomposition of large sparse asymmetric matrices, such as the Jacobian matrices that arise in the Newton iterations using finite-element methods. The speed increase associated with the use of the parallel algorithms will make three-dimensional calculations feasible.

Publications

Bennett, M.J. and Brown, R.A., "Cellular dynamics during directional solidification: interactions of multiple cells," Phys. Rev. **B89**, 705-723 (1989).

Kim, D.-H. and Brown, R.A., "Models for convection and segregation in the growth of HgCdTe by the vertical Bridgman method," J. Cryst. Growth **96**, 609-627 (1989).

Tsiveriotis, K. and Brown, R.A., "Bifurcation structure and the Eckhaus instability," Phys. Rev. Lett **63**, 2048-2051 (1989).

Duranceau, J.L. and Brown, R.A., "Convection in earthbound and microgravity floating zones," in *Proceedings Third International Colloquium on Drops and Bubble*, Volume 197 (T. Wang, ed.), AIP 1989, pp. 133-144.

Brown, R.A., "Theory of transport processes in single crystal growth from the melt," in *Chemical Engineering in Microelectronics Processing*, ACS Advances in Chemistry Series Vol. 222, 1989, pp. 35-104.

Krylidis, A., Brown, R.A. and Walker, J.S., "Retardance of particle sedimentation in an electrically conductive liquid by an aligned magnetic field," *Phys. of Fluids* 2, 2230-2240 (1990).

Kim, D.-H. and Brown, R.A., "Transient simulation of convection and solute segregation of GaAs growth in a vertical gradient freeze furnace," *J. Cryst. Growth*, 1990, in press.

Brown, R.A. and Kim, D.H., "Modelling of directional solidification: from Scheil to detailed numerical simulation," *J. Cryst. Growth*, 1990, in press.

Kim, D.-H. and Brown, R.A., "Modelling of transients in growth of HgCdTe by the vertical Bridgman technique," *J. Cryst. Growth*, 1990, (submitted).

Lee, C.T., Ramprasad, N. and Brown, R.A., "Two-dimensional cellular structures in the solidification of $\text{CBr}_4\text{-Br}_2$: comparison of calculations with experiments," *J. Cryst. Growth*, 1990 (submitted).

Bennett, M.J. and Brown, R.A., "Nonlinear Dynamics in Periodically Repeated Sets of Directional Solidification Cells," *Phys. Rev. B*, 1991, submitted.

Brown, R.A. "Perspectives on Integrated Modeling of Transport Processes in Semiconductor Crystal Growth," in *Advanced Heat Transfer in Manufacturing and Processing of New Materials*, Hemisphere Press, 1991, in press.

Lee, J.T.C. and Brown, R.A. "The Planar to Cellular Transition and the Long Time Scale Dynamics of Pattern Formation During Thin-Film Directional Solidification," *Materials Research Society*, 1991, in press.

Interfacial Phenomena

NASA Lewis Research Center
Dr. A.T. Chai
Mr. J.B. McQuillen
Mr. M.M. Weislogel
In-House

Contact Angle Measurements-A. Chai

The objective of this research is to experimentally determine the feasibility of utilizing the constant curvature of a liquid-vapor interface encountered at low Bond number (i.e., low-gravity) conditions to provide accurate measurements of contact angles. A special sample container and rig for use in the 5 second Zero-Gravity Facility at Lewis has been designed and fabricated. Preliminary testing has demonstrated some potential in the approach and further revisions are planned for future

Two Phase Flow Through Fittings-J. McQuillen

The objective of this study is to examine the effects of variable conduit cross section (tubing diameter and direction) on two phase flow behavior in a reduced gravity environment. Tests have focused on the 0.95 to 2.54cm ID tubing expansion (3/8 diameter ratio), primarily examining the effect of the initial state of the test section. The test section in previous experiments was "dry" prior to the start of the low gravity test and showed the formation of a two phase jet. Tests were also conducted where the test section was completely filled with liquid at the start of the low gravity test. During the limited time of these tests, the liquid was displaced by gas in the two phase jet and began to approach the conditions seen when the test section was initially dry. Plans to include the effect of liquid properties, a 3/4 diameter ratio expansion, and improvements in photographic quality are being implemented.

Capillary Phenomena-M. Weislogel

This research encompasses several tasks. (1) A test apparatus, which will be devoted to the study of surface stability, has been designed and is being fabricated. The stability limits for numerous container geometries and fluid properties will be quantified as both steady and unsteady disturbances, acting along or at an angle to the principle axis of the container, are applied. (2) A series of tests are being performed to note the terminal velocity of a liquid slug driven entirely by capillary forces. These forces are produced by a discontinuous wall wetting condition via a surface coating. Drop tower tests are being conducted as relatively large cylindrical tubes need to be employed for observation in the Lewis 2.2 second drop tower. (3) Surface tension measurements are being conducted on an inverted liquid-vapor interface using a laser light scattering technique. The measurement is being pursued to investigate the effects of gravity on the value of the surface tension. Preliminary results reveal a small yet detectable effect. These results could be significant and a technical note is being prepared for publication.

Publications

Weislogel, M.M., Ross, H.D., "Surface Reorientation and Settling in Cylinders upon Step Reduction in Gravity", Microgravity Sci. Technol. III, 1 (1990).

Weislogel, M.M., Ross, H.D., "Surface Settling in Partially Filled Containers upon Step Reduction in Gravity", NASA TM-103641, November, 1990.

Fluid Interface Behavior under Low- and Zero-Gravity Conditions

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Paul Concus
Robert Finn (Stanford University)
NAG3-1143

Objectives: The general objective of this research is to gain better mathematical understanding of the physical behavior of fluids partly filling a container or otherwise in contact with solid support surfaces, when capillary forces predominate. Closely interrelated with the mathematical and computational studies are current and planned ground-based and in-space microgravity experiments.

Research Task Description: Work currently is directed (a) toward the realization of experiments designed to observe actual behavior of equilibrium fluid configurations in "exotic" containers for which exact theory predicts an entire continuum of symmetric surface interfaces, but for which it can be shown that no symmetric interface can be stable. Our second (and independent) direction (b) is toward the design of experiments for very precise measurement of contact angle; these latter experiments are intended also as a test of the physical validity of the concept of contact angle, as envisioned by the classical Young-Gauss theory.

The specific design and construction of the experimental apparatus for item (a), scheduled for flight on USML-1, is being carried out by M. Weislogel at NASA Lewis Research Center, and the experimental apparatus for item (b), scheduled for flight on IML-2, is being constructed under the aegis of the European Space Agency in collaboration with D. Langbein, U. Hornung and M. Haynes. In both cases our responsibility rests primarily with the mathematical and computational theoretical underpinnings.

Progress to Date: A systematic numerical calculation of the exotic containers has been completed over a range of parameters of physical interest. Preliminary drop-tower experiments have been carried out by M. Weislogel at the NASA Lewis Zero Gravity Facility, and in some of the experiments the fluid reoriented from its initial symmetric configuration during the period of free fall to one that was not symmetric, in corroboration of the mathematical theory. The time scale was too short to obtain scientifically definitive results, but the experiments provide needed information for the design of longer-duration microgravity experiments in space. Numerical calculations to seek energy-minimizing configurations in the exotic containers were initiated in collaboration with M. Callahan, and preliminary results look remarkably similar to the surface indicated in the drop-tower experiments.

In connection with item (a) above, joint work with T.I. Vogel on liquid bridges between parallel plates was carried out. We have proved that for any contact angle the greatest lower bound on fluid volumes at which such a bridge can be stable always exceeds the value that occurs for contact angle 90 deg. Since in this latter case the critical volume is known explicitly, we obtain a working estimate valid for any contact angle. In this way we are able to design an exotic container so as to exclude the occurrence of (unwanted) liquid bridges between the top and bottom surfaces. The investigation is continuing with a view to characterizing what happens when the contact angles on the two surfaces differ.

With regard to the forthcoming space experiments, an estimate was required of the critical contact angle for a cylindrical container with rectangular section whose corners are rounded by circular arcs of prescribed radius. The critical angle is determined by the property that a (wetting) solution surface of the capillary equation simply covering the base exists if and only if the contact angle is larger

that a critical value. We were able to apply our methods developed earlier and characterize all subsidiary extremals, to give an exact result for the needed estimate.

For item (b) above, one of the two methods proposed for contact angle measurement is based ultimately on a discontinuous behavior of capillary surfaces in wedge domains. In adapting our earlier ideas to the needs of experiment design, we have been led to consider a cylindrical capillary tube whose section is a "near rhombus". An initial estimate for contact angle is to be made under terrestrial conditions, and the sectional angles adjusted accordingly. If the estimate is correct, the fluid height of any capillary surface in the tube will fall to zero (in zero g) over a region of the base, and the fluid will move to the more acute corner. If too high, the fluid will fill out both corners, and if too low the surface height will remain between explicitly known positive bounds. The method does not require precise observation of the surface in the corners. It is anticipated that very good accuracy will be obtained for contact angles greater than about 45 degrees for the wetting case.

Our expectation is that the above method will yield accuracy that is significantly better than current procedures, for values of the contact angle as above. For smaller contact angles another procedure is contemplated for accurate measurement that is based on the special properties of a "two-circle" geometry. We have initiated numerical calculations to solve the capillary equation in this geometry, and preliminary calculations for certain values of the parameters have indicated the desired nearly-discontinuous behavior.

We have initiated a study with a student, B. Fischer, with a view to characterizing other geometries adapted to precise contact angle measurement, using in yet a different way our earlier results. The initial progress has been very promising. It appears likely that it will be possible to characterize (even explicitly) a geometry that admits an entire continuum of "subsidiary minimizers" for prescribed contact angle; when applied to the measurement techniques, the result may yield a more precise estimate than the present procedure, for arbitrarily small contact angle and with less need for sophisticated computer calculations.

Publications

Callahan, M, "Some numerical solutions of capillary equations in exotic containers," Report LBID-1703, Lawrence Berkeley Laboratory, University of California, 1991.

Concus, P. and Finn, R., "Capillary surfaces in microgravity," in *Low-Gravity Fluid Mechanics and Transport Phenomena*, Volume 130 (J. N. Koster and R. L. Sani, eds.), AIAA, 1990, pp. 183-206.

Concus, P. and Finn, R., "Dichotomous behavior of capillary surfaces in zero gravity," Microgravity Sci. Technol. 3, 87-92 (1990).

Concus P. and Finn, R., "Nonuniqueness and uniqueness of capillary surfaces," in Geometric Analysis and Computer Graphics, Volume 17 (P. Concus, D. Hoffman, and R. Finn, eds.), Springer-Verlag, 1991, p.63.

Concus P., and Finn, R., "Exotic containers for capillary surfaces," *J. Fluid Mech.*, 1991, (to appear).

Presentations

Bank, R.E., Concus, P., and Finn, R., "Numerical study of nearly discontinuous behavior of certain capillary surfaces," *American Mathematical Society 97th Annual Meeting*, San Francisco, January 1991; Amer. Math. Soc. Abstracts 12 (1991), p. 162.

Callahan, M., Concus, P., and Finn, R., "Energy minimizing capillary surfaces for exotic containers," *American Mathematical Society 97th Annual Meeting*, San Francisco, January 1991; Amer. Math. Soc. Abstracts 12 (1991), p. 162.

Concus, P., Finn, R., and Weislogel, M., "Drop-tower experiments for capillary surfaces in an exotic container," *29th Aerospace Sciences Meeting*, Reno, January 1991, Paper No. AIAA 91-0107.

Finn R., and Vogel, T.I., "The volume infimum for stable liquid bridges," *American Mathematical Society 97th Annual Meeting*, San Francisco, January 1991; Amer. Math. Soc. Abstracts 12 (1991), p. 137.

Finn, R., "Three lectures on capillarity theory," *International Semester on Partial Differential Equations*, Warsaw, Poland, September 1990.

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Convective and Morphological Stability During Directional Solidification

National Institute of Standards and Technology

Dr. S. R. Coriell

Dr. G. B. McFadden

Dr. J. R. Manning

Objectives: The general aim of this task is the study of the fluid flow, solute segregation, and interface morphology which occur during directional solidification, including effects of gravity and microgravity. Control of solute segregation during solidification will allow preparation of materials with optimum properties. Space flight experiments, designed to determine cellular wavelengths as a function of growth conditions, are planned in collaboration with J. J. Favier, A. Rouzaud, and D. Camel of the Centre d'Etudes Nucleaires de Grenoble utilizing the directional solidification furnace being developed by the MEPHISTO project.

Research Task Description: The main focus of this task is the interaction of fluid flow in the melt with the crystal-melt interface, and the solute segregation which is controlled by interface morphology and fluid flow. In the absence of fluid flow, the conditions for morphological instability during directional solidification of an alloy at constant velocity are well established. However, for processing conditions for which instability occurs, the resulting non-planar interface morphologies (cellular or dendritic) are an active area of current research. Although progress has been made in calculating cellular morphologies, the question of wavelength selection is unresolved, and definitive experiments (without convection) are needed to provide guidance and a benchmark for theoretical developments. Numerical algorithms to calculate cellular morphologies in the absence of convection are being developed. Linear stability analyses of the effect of various types of fluid flow on the onset of morphological instability are carried out in order to delineate the role of convection. Fluid flow in the melt is calculated by a time-dependent, two-dimensional finite difference algorithm as a function of the gravitational acceleration. This allows prediction of the differences between experimental results obtained on earth and in space. The effect of time-dependent gravitational accelerations (g-jitter) is studied both by linear stability analyses and numerical solution of the nonlinear fluid flow equations. Since the MEPHISTO furnace uses electrical pulsing and Seebeck measurements, research on the effect of electrical currents on the solidification process and solute redistribution is also underway.

Progress to Date: In collaboration with R. F. Sekerka of Carnegie-Mellon University, we have carried out a linear morphological stability analysis of a planar interface during directional solidification of a binary alloy for the case of a crystal having an anisotropic thermal conductivity. We have calculated a dispersion relation which shows that the onset of instability depends on the orientation of the growth direction with respect to principal crystallographic axes and on the orientation of the wavevector of the perturbation. The onset of instability can be either oscillatory (travelling waves) or non-oscillatory in time. For growth along a principal axis of the crystal there is an exchange of stabilities, and the onset of instability is non-oscillatory. For a uniaxial crystal, the dispersion relation has been explored in detail, and numerical results obtained for an alloy of 0.78 atomic percent bismuth in tin. For low growth velocities the onset of instability is non-oscillatory and occurs for perturbations having a wavevector that lies along a principal crystallographic axis.

During directional solidification of a binary alloy at constant velocity, thermosolutal convection may occur due to the temperature and solute gradients associated with the solidification process. For vertical growth in an ideal furnace (lacking horizontal gradients) a quiescent state is possible. For a range of processing conditions, the thermal Rayleigh number is sufficiently small that the stabilizing role of the thermal field during growth vertically upwards may be neglected, and only solutal

convection need be considered. In collaboration with B.T. Murray of NIST, the effect of a time-periodic vertical gravitational acceleration (or equivalently vibration) on the onset of solutal convection is calculated based on linear stability using Floquet theory. A stable base state can be destabilized due to modulation, while an unstable state can be stabilized by modulation. The flow and solute fields show both synchronous and subharmonic temporal response to the driving sinusoidal modulation. Time-dependent numerical calculations in two dimensions are consistent with the linear stability analysis, and allow a description of the nonlinear behavior of the system.

In collaboration with M.E. Glicksman and M.E. Selleck of Rensselaer Polytechnic Institute and B.T. Murray of NIST, the linear stability of circular Couette flow between concentric infinite cylinders has been considered for the case that the stationary outer cylinder is a crystal-melt interface rather than a rigid surface. A radial temperature difference is maintained across the liquid gap, and equations for heat transport in the crystal and melt phases are included to extend the ordinary formulation of this problem. The stability of this two-phase system depends on the Prandtl number. For small Prandtl number the linear stability of the two-phase system is given by the classical results for a rigid-walled system. For increasing values of the Prandtl number, convective heat transport becomes significant and the system becomes increasingly less stable. Previous results in a narrow-gap approximation have been extended to the case of a finite gap, and both axisymmetric and nonaxisymmetric disturbance modes have been considered. The two-phase system is more stable to nonaxisymmetric modes with azimuthal wavenumber $n = 1$; the stability of these $n = 1$ modes is sensitive to the latent heat of fusion.

Publications

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Modeling of Coalescence, Agglomeration and Phase Segregation in Microgravity Processing of Bimetallic Composite Materials

University of Colorado at Boulder

Dr. Robert H. Davis

NAG3-993 (NASA Contact: R. Balasubramanian, LeRC)

February 2, 1989-February 1, 1991

Objectives: The primary objective of this research is to develop models to predict drop-size-distribution evolution due to droplet collisions and coalescence during processing within the miscibility gap of bimetallic liquid-phase-miscibility-gap materials. The individual and collective action of gravitational and nongravitational mechanisms on the relative motion and coalescence of drops are considered.

Research Task Description: When bimetallic liquid-phase-miscibility-gap materials, which are thought to have a variety of desirable properties, are cooled through the miscibility gap, droplets rich in one of the metals form in the liquid matrix rich in the other metal. Droplet coalescence and phase segregation then occur due to buoyancy and to thermocapillary and other nongravitational mechanisms. In order to gain a predictive understanding of these phenomena, population dynamics models are used to follow drop-size distribution evolutions in time as the droplets grow due to collision and coalescence. Continuous drop size distributions are discretized into a large number of categories. Drops of a given mass are destroyed by coalescing with other drops and are formed by the coalescence of smaller drops. The population dynamics model tracks the formation and destruction of drops in each size category.

The relative motion of drops which gives rise to their collision and coalescence is considered to occur by gravity sedimentation, Marangoni migration, Brownian motion, and bulk flow. These collision mechanisms are considered either individually or collectively in the population dynamics models. In general, different mechanisms dominate for different processing conditions, materials properties, and drop-size ranges.

The collision kernels appearing in the population dynamics models require expressions for the collision rate between drops of two different sizes. Classical expressions attributed to Smoluchowski are improved to include attractive, repulsive, and hydrodynamic interactions between drops. In particular, trajectory calculations are used to predict collision efficiencies, which represent the ratio of the collision rate with these interactions to the Smoluchowski collision rate without these interactions, as functions of the size ratio, viscosity ratio, and other relevant dimensionless parameters.

Progress to Date:

1. A computer program has been completed for solving the population dynamics model to follow droplet size evolutions with time in homogeneous dispersions due to collisions arising from gravity sedimentation, Marangoni migration, and/or Brownian motion. Some of the key results are that a bimodal initial distribution will exhibit much more rapid coalescence due to gravity sedimentation or Marangoni migration than will a unimodal initial distribution, a unimodal initial distribution will evolve into a bimodal distribution and then into a shifted and broadened unimodal distribution, and that coalescence may be greatly reduced by antiparallel alignment of the gravity vector and the temperature gradient.

2. Collision efficiencies for Brownian motion and gravity sedimentation for drops having a range of viscosity and radius ratios have been computed both in the presence and absence of attractive forces. A key result is that, in contrast to rigid particles, liquid drops have nonzero collision efficiencies in the absence of attractive forces

3. Theoretical work is in progress on flow-induced collisions, collision efficiencies for Marangoni migration, spatial variations in drop-size distributions, and macroscopic phase segregation.

4. In related theoretical work, the natural evolution of the approach and deformation of two drops driven together by gravity and/or van der Waals forces has been analyzed by regular and singular asymptotic expansions. In the absence of attractive forces, the drop deformation will prevent coalescence.

5. In related experimental work, drop size distributions in transparent immiscibles are being followed with time by holography as coalescence occurs due to gravity, Brownian, and Marangoni motion.

Publications

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Numerical Simulation of Fluid Transport Phenomena

Lewis Research Center
Dr. J. C. Duh
In-House

Objectives: The main objective of this program is to use numerical simulation to enhance the fundamental understanding of the fluid transport phenomena of interest to the microgravity science and applications program.

Research Task Description: Two major areas of interest to this program are buoyancy driven flow (Rayleigh transport) and surface tension driven flow (Marangoni transport). In each of these two areas, both convection and thermal instability are investigated. The combined effect of buoyancy and surface tension on the fluid transport is another theme area to be researched.

Progress to Date:

(1) On the subject of Rayleigh convection, the onset of secondary cells in an enclosure with differentially heated side walls and insulated top and bottom surface has been studied. The critical Rayleigh number (Ra_c) for the onset of secondary cells have been obtained for a wide range of aspect ratio (Ar) and Prandtl number (Pr). The results suggest a different relation between Ra_c and Ar than what has been previously suggested by experimental studies. When $Ar < 1$, Ra_c increases with Ar , but when $Ar > 1$, Ra_c decreases as Ar increases. The numerical results also indicate that at extreme Ar 's, the secondary cells may always exist unconditionally.

(2) On the subject of surface tension instability, a numerical mechanism has been tested successfully to determine the critical Marangoni number (Ma_c) for the onset of flow. The numerical procedure consists of the following steps: (i) generate a temperature disturbance at the free surface and calculate the temperature distribution in the bulk fluid when subject to such a disturbance, (ii) calculate the velocity disturbances resulting from such a temperature disturbance, (iii) combine the temperature and velocity disturbances as the initial data for the time integration of the resulting flows, if the flow is subdued and returned to quiescent state, then it is a stable system; if the flow reaches certain steady state without returning to quiescent state, then it is in supercritical region. The preliminary results obtained so far indicate that an initial temperature disturbance of a step-change nature will be able to cover a wide enough range of wave numbers and will give the lowest Ma_c as compared to other forms of disturbance. The amplitude of the initial disturbance does not affect the Ma_c and the final flow pattern and strength, a finding which is very encouraging in the pursue of direct numerical simulation of the Benard cells.

Publication

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Two Phase Gas Liquid Flow under Reduced Gravity Conditions

University of Houston
Professor A. E. Dukler
NAG 3-510 (NASA Contact: J. McQuillen, LeRC)
December 1888 - December 1991

Objectives: Gravity is the dominant force during gas-liquid flow in conduits as a result of the presence of the free surface. The program consists of both experimental and modelling studies. Learjet trajectories are used to generate reduced gravity data in a specially designed test rig mounted in the plane. The objectives include determining the detailed characteristics of the flow such as time dependent pressure gradients and void fractions, bubble and slug sizes and flow patterns. Based on the insight provided by the data it is the objective to develop physically based mathematical models which provide general techniques for predicting two phase flow characteristics thus avoiding the use of empirical correlations as has largely been the case in the past.

Research Task Description: Experimental: The test section consists of a 1.27 cm diameter tube 114 cm long mounted in a test loop which provides metered gas and liquid and is equipped to measure the pressure gradient, void fraction and liquid film thickness as a function of time at 250Hz each. 400 frames/s cameras are used to observe the flow and these films are analyzed to extract information on the flow pattern, slug and bubble lengths for slug flow, film thicknesses and entrainment during annular flow, bubble size during dispersed bubbly flow and propagation velocities. The work also includes the process design of a heat transfer test loop to be flown on the KC135.

Modelling: The long term research tasks calls for models to be developed for flow pattern transition, slug flow hydrodynamic characteristics (pressure drop and flow geometry), annular flow frictional losses and interfacial characteristics, and bubble size and distribution.

Progress to Date: Experimental: A total of 133 trajectories have been completed, 99 of these were taken within 0.02g and 34 at approximately 0.17g to simulate moon gravity. 85 of these runs were carried out with the air-water system, 27 with a glycerine solution having elevated viscosity and 21 with a surfactant solution having low surface tension. Detailed analysis of the data is now about 75% complete. Existing two phase flow correlations used at 1 g have been extensively tested against the data and their inadequacies demonstrated.

Modelling: A mathematical model has been completed which can be used to construct zero g flow pattern maps given the fluid properties and tube size. A model which predicts the hydrodynamic characteristics of slug flow is about 85% complete.

Molecular Dynamics of Fluid-Solid Systems

City College of New York and Pennsylvania State University
Prof. Joel Koplik
Prof. Jayanth R. Banavar
NAG3-1167

Objectives: Several interesting unresolved problems in fluid mechanics occur when the process is controlled by a microscopic region which is too small to be described faithfully by the continuum Navier-Stokes equations, or alternatively when the appropriate boundary conditions are unknown. Examples include the moving contact line singularity arising when a viscous fluid displaces a second immiscible fluid along a solid substrate, the late stages in the coalescence or fission of liquid drops, the detailed local dynamics of the spreading of liquids across a solid surface, and the freezing and structure of liquids in microporous systems. We propose to use molecular dynamics numerical simulations to study these processes. In so doing, the correct molecular behavior is built into the calculation, and the result is a relatively unbiased numerical experiment which will elucidate the above questions.

Research Task Descriptions: Beginning with standard molecular dynamics computer codes, the first new ingredient required is a molecular solid bounding wall with realistic thermal and structural properties. With this in hand, dynamics in microporous systems can be investigated by controlling the operating conditions via solid bounding walls, mimicking laboratory experiments, but with vastly higher resolution. The same type of wall can be used to examine drop spreading on substrates, and to construct a computer "four-roller mill", which will provide controlled external flow conditions for drop dynamics studies. The numerical simulations give immediately the instantaneous configurations and velocities of the fluid(s), while density and temperature profiles, average Eulerian velocity and stress fields and other continuum quantities can be obtained by averaging.

Progress to Date: A suitable molecular wall has been developed, using a Lennard-Jones potential adjusted to maintain the solid atoms close to their crystalline equilibrium positions. Using this wall, we have observed a novel two-step ordering process in freezing in microporous systems (e.g. Vycor), wherein the liquid first forms layers parallel to bounding walls, and subsequently each layer orders and sharpens. This picture is in agreement with experiment as far as measurements have been made. The effects of channel size, quench procedure, wall-liquid interaction and wall roughness have been examined. Simulations of the fission of liquid menisci in pendant drops and free liquid threads have been conducted, which are in qualitative accord with continuum expectations. Detailed quantitative analysis is in progress. Initial drop spreading simulations likewise behave roughly as expected, and the changes in behavior as a function of the liquid-solid interaction are being studied now.

Publications

W.-J. Ma, J.R. Banavar, and J.Koplik, "Dynamics of Freezing in Confined Geometries," Phys. Rev. Lett., 1990 (submitted).

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Suppression of Marangoni Convection in Float Zones by a Gas Jet

David Taylor Research Center
Hans J. Lugt, Code 1205
Samuel Ohring, Code 1281 .
Work Order No. C-32007-M

Objectives: According to the amendment of September 10, 1990 to project C-32007-M, the project objectives are: Computational study of high Marangoni flows in a silicon float zone and determination of the critical Marangoni number for the oscillatory convection to occur.

Research Task Description: The onset of Marangoni convection in the float zone of liquid silicon shall be studied from a state at rest in the absence of gravity. This time-dependent flow problem shall be solved numerically with the aid of the Navier-Stokes equations for an axisymmetric flow with nonlinear free-surface conditions. On this free surface either the temperature gradient will be generated by heat transfer and radiation from a heater, or the temperature itself will be prescribed.

Progress to Date: A Navier-Stokes computer program for a general axisymmetric float-zone model has been developed with some preliminary results. Most important is the result that an axisymmetric float zone with $Ma = 10400$ could not be induced to oscillate after the flow field, which was initially symmetric, was disturbed. During the entire time span covered, the free surface deforms only slightly so that the assumption of a flat undeformable free surface appears justified. However, the slight deformation does not exclude the possibility that a deformable free surface can induce instability. It is planned to compute flows of still higher Marangoni number with an improved numerical code.

Stability and Instability of Thermocapillary Convection in Models of the Float-Zone Crystal Growth Process

Georgia Institute of Technology

Professor G. Paul Neitzel

Professor Daniel F. Jankowski, Arizona State University

Professor Hans D. Mittelman, Arizona State University

NAG 3-568 (NASA Contact: R. Balasubramaniam, LeRC)

Objectives: The objectives of this research are an investigation of the stability properties of thermocapillary convection in a model of the float-zone crystal growth process. Energy stability limits provide sufficient conditions for stability of a basic state, while linear-stability limits provide sufficient conditions for instability. The successful computation of such a limit for an actual float-zone basic state would identify conditions under which oscillatory convection (and hence undesirable striations in the final material) can be avoided.

Research Task Description: The research associated with this project is being carried out in a variety of related, complementary areas: (1) extension of energy-stability results computed for thermocapillary convection in a half-zone assuming axisymmetric disturbances to include three-dimensional disturbances; (2) computation of linear-stability properties of the same basic state; (3) application of energy-stability theory to a half-zone basic state with a deformable free surface; (4) consideration of alternate heat-transfer conditions at the free surface; and (5) direct numerical simulation of oscillatory thermocapillary convection in a half zone.

Progress to Date: The extension of energy-stability theory to include three-dimensional disturbances has been accomplished. The code was checked extensively against published results for the stability of a state of pure conduction in a cylinder heated from below. Thermocapillary convection results have been obtained for a variety of aspect ratios and compared with data from recent laboratory experiments of Velten, Schwabe and Scharmann.

Linear-stability theory has likewise been applied to the heated cylinder problem in order to check the behavior of the numerical algorithms being employed. The application of the theory to the half-zone has been accomplished and computations are underway. Two numerical methods are being utilized to see which allows the more efficient determination of results. The numerical problem associated with the linear theory is more difficult than that for energy theory due to the lack of symmetry associated with the linear-stability problem.

Work on the application of energy-stability theory for free-surface deformation has begun anew with a new graduate research assistant, and work on the consideration of alternate free-surface heat-transfer conditions and direct numerical simulation will commence during Winter Quarter 1991.

Publications

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Presentations

Law, C.C., Jankowski, D.F., and Neitzel, G.P., "Energy-Stability Limits for the Heated-Cylinder Problem with Axisymmetric and Non-axisymmetric Disturbances," *Sixth Arizona Fluid Mechanics Conference*, Tempe, February 23-24, 1990.

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Disorder-Order Transitions in Colloidal Suspensions: Computer Simulations and Experimental Observations

Princeton University

William B. Russell

Pablo G. Debenedetti

NAG3-859

January 20, 1988 - February 19, 1991

Objectives: The goal of this work is to understand the rate and mechanisms of formation of ordered, crystalline structures in concentrated colloidal suspensions, experimentally and computationally. Experiments will be aimed at developing a technique for the production of macroscopic single crystals by the application of periodic electric fields. From a scientific viewpoint, the dynamics of this phase transition has been largely unexplored. Practically, understanding the disorder-order transition is of importance in areas such as ultrafiltration and ceramics fabrication from submicron particles via colloidal processing routes.

Research Task Description: Our most important experimental task is to grow macroscopic single crystals by inducing order in the first few layers via an external field to provide a pattern for subsequent crystal growth. Our plans have shifted from the creation of interdigitating electrodes to either a diffraction pattern created by crossed laser beams or simple physical confinement of a monolayer of particles. With this funding terminating, the effort will be absorbed into our other NASA grant.

Statistical Mechanics of Fluids: the Effects of an External Gravitational Field

NASA Lewis Research Center
Dr. R. E. Salvino, Sverdrup Technology
Dr. R. A. Wilkinson, NASA LeRC
In-House

Objectives: The objective has been to establish a formal representation of gravitational contributions to equilibrium and nonequilibrium thermophysical properties of fluids starting from a classical statistical mechanical foundation. From that representation an identification of strength of effect and the most fruitful properties to explore is intended. The final goal is to compute and experimentally verify observed effects.

Research Task Description: The work has included molecular dynamics simulations and analytical efforts. This past year dealt mostly with the analytical activity. The classical mechanics of many particles was used starting from a Hamiltonian for fluid atoms or molecules, adding an extra energy term for the external gravitational field, and deriving equilibrium thermodynamic properties via partition functions and differential forms of the free energies. In the non-equilibrium case, particle equations of motion provided velocities that were time auto-correlated to project out transport properties. The resulting analytical representations provide one basis to suggest the strength of gravitational effects.

Progress to Date: Two publications present the results of the analytical work. A challenge is to fund an experimental system to test the results and/or execute a molecular dynamics simulation to confirm predictions.

Publications

R. E. Salvino, "Equilibrium Statistical Thermodynamics of a Many--Particle System Coupled to an External Scalar Field," Phys. Rev. A **41**, 4236 (1990).

R. E. Salvino, "The Newtonian Mechanics of a Many--Particle Assembly Coupled to an External Body Potential," Phys. Rev. A (accepted).

The Roles of Fluid Motion and other Transport Phenomena in the Morphology of Materials

Princeton University

Dr. D. A. Saville

NAG 3-447 (NASA Contact: Dr. Robert Snyder, MSFC)

Objectives: The objective is to find out how certain transport phenomena influence the morphology of crystalline materials. Two problems are under study: one deals with the effects of convection on the crystallization of pure materials, the other with the crystallization of proteins from solution. In the first study we are interested in how convection alters relations between undercooling and the speed and stability of growth. In the second, we seek to find out why protein crystals grow as slowly as they do and how crystal morphology depends on the growth rate and crystal size.

Research Task Descriptions:

Crystal Growth in the Presence of Convection

A computation scheme has been developed which simulates the evolution of a needle-shaped crystal in an undercooled melt when convection is present. The computer program will be exercised to explore a wider range of undercoolings, flow strengths, and material properties. The algorithm will also be expanded to permit better resolution of the tip region and to allow for crystal anisotropy.

Protein Crystal Growth

Experimental apparatus has been constructed to record the growth process with a digital imaging system. Using model proteins we will study the relations between crystal growth rate, size, and quality.

Progress to Date: Theoretical work on calculating the effects of convection continues. At present we are engaged in extending the computation of "microscopic solvability" to include the effects of convection. The experimental work on lysozyme crystallization under quiescent and flow conditions is complete and the data are being analyzed.

Publications

P. J. Beaghton and Saville, D.A., "Growth of Needle-Shaped Crystals in the Presence of Convection," Phys. Rev. A 37, 3423-3430 (1988).

Saville, D.A., "The Roles of Transport Phenomena in Protein Crystal Growth," J. Cryst. Growth, in press.

Capillary Containment of Liquids in a Microgravity Environment: Shear-stabilization and Rupture

Cornell University

Dr. P.H. Steen

NAG3-801 (NASA Contact: L.H. Dill, LeRC)

June 1, 1987 - September 30, 1990

Research Task Description: In the low-gravity environment of a space-laboratory, without the stabilizing influence of the gravity of our experience, free or partially-free bodies of liquid must be stabilized by other means. Surface tension is the obvious candidate. The influence of motion on the containment by surface tension is important to a wide variety of processing applications (materials and/or chemical). It turns out that this influence can have surprising effects. In particular, we study the influence of liquid motion on the capillary instability. We ask two contrasting questions: can motion enhance the stability of a configuration (containment) and what motions are generated when a configuration is unstable (rupture)? The answer to the first question is "yes" and we explore the range of conditions under which stabilization can occur. The second question is important, for example, in determining the size of satellite droplets generated during breakup.

Progress to Date:

(i) has discovered and mapped out the windows in parameter space where hydrodynamic shear forces can stabilize capillary break-up in long cylindrical interfaces according to linear stability theory in a variety of contexts: rod flow (isothermal) and thermocapillary-driven, tube flow, and core-annular rod flow (in preparation). In particular, the physical mechanism of stabilization has been identified.

(ii) has designed, built, and tested an apparatus capable of exploring the influence of shear on capillary instability in a parameter range where theory suggests stabilization may occur.

(iii) has developed a simpler analog experimental system, the soap-film bridge, by means of which many of the fundamental influences of motion on stability may be observed and studied. The soap-film bridge has already illustrated details of the rupture phenomenon never before documented.

Publications

Russo, M.J., and P.H. Steen, "Shear-stabilization of the Capillary Breakup of a Cylindrical Interface", Phys. Fluids A 1:, 1926-1937 (1989).

Steen, P.H., "Capillary Containment and Collapse in Low Gravity: Dynamics of Fluid Bridges and Columns", in *Proceedings of the 5th International Colloquium on Free Boundary Problems*; Montreal, Canada, June 1990, in press.

Dijkstra, H.A., and P.H. Steen, "Thermocapillary Stabilization of the Capillary Break-up of an Annular Film of Liquid", J. Fluid Mech., in press.

Dijkstra, H.A., "The coupling of Marangoni and Capillary Instabilities in an annular Thread of Liquid", J. Colloid Interface Sci., 136, 151-159, (1990).

Physical Phenomena in Containerless Glass Processing

Clarkson University
Dr. R. Shankar Subramanian
Dr. Robert Cole
NAS8-32944 (NASA Contact: R. Daugherty, MSFC)

Objectives: The objective of this investigation is to develop an understanding of fluid motion and bubble and droplet motion and interactions when drops containing bubbles are subjected to stimuli such as surface tension gradients, rotation, expansion and contraction, and oscillation.

Research Task Description: The research task for this period involved conducting experimental studies of bubble/drop motion in rotating liquid bodies. Supporting theoretical models were also to be developed for comparison with the data.

Progress to Date: Experiments were performed on the motion of bubbles contained in freely suspended rotating drops. The drops first move to the rotation axis during which period the bubbles are normally found to stay in their relative locations within the drops. However, upon reaching the axis of rotation, the drops reach a rotation speed close to that of the surrounding fluid, and the bubbles are found to migrate inward toward the rotation axis. The data have been compared with predictions from theoretical models.

Publications

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The Study of Electromagnetically-Driven Flow in Aqueous Systems Using Laser Velocimetry

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Professor Julian Szekely
David Forrest
NAGW-1762 (NASA Contact: M. Lee, HQ)

Objectives: The objective of this research is to develop a numerical model to predict 3-D magnetohydrodynamic (MHD) fluid flow and to test the numerical model against experimental measurements. The experimental design in this proposal is intended to be a prototype for future equipment for Learjet low gravity and Shuttle microgravity experiments. The specific goals of this research are to: (1) develop a numerical model to predict heat flow, velocities, and turbulence in 3-D Cartesian coordinates for MHD flow of an aqueous electrolyte in an enclosed cavity, driven by alternating current passing between two electrodes, (2) build an experimental apparatus to measure MHD flow in this system; the design will be optimized based on initial numerical calculations, (3) measure velocities and turbulence using a laser Doppler velocimeter, (4) compare the computed results with the experimental measurements, (5) determine the suitability of this system for Learjet and Shuttle flights.

Research Task Description: The proposed system, with the general design consisting of an applied current between two electrodes of unequal size, is applicable to a variety of materials processing operations with similar geometries: electrosag refining, direct arc electric furnace steelmaking, the Hall-Heroult cell, and electrosag welding. This experimental work will quantify how accurately we can predict transport phenomena in these materials processing operations, and help us to learn how our models can be improved. The use of 3-D Cartesian coordinates will allow us to model complex geometries. The use of a transparent system will allow us to take full advantage of the powerful data acquisition capabilities of laser Doppler velocimetry to better study the turbulence structure.

Progress to Date: We have designed a novel apparatus to generate turbulent MHD flow in an aqueous system. Using PHOENICSTM and our own electromagnetic solver, we have developed both 2-D cylindrical and 3-D Cartesian codes to calculate MHD-driven flow in our system design. We can calculate the applied electric field from arbitrary electrode configurations, the applied magnetic field from arbitrary coil configurations, and the fluid flow, turbulence, and heat transfer in the MHD cell. The code accounts for spatial variation in electrical conductivity and viscosity. We have optimized the design of the MHD cell using this code and are now in the process of constructing the experimental apparatus. The code we have developed has already proven useful in studying metallurgical systems such as smelters and rheocasters.

Drop Coalescence Studies

Vanderbilt University
Professor Taylor G. Wang
Dr. A.V. Anilkumar
Dr. C.P. Lee

Objectives: The objective of this investigation is to understand the detailed mechanics of the coalescence of liquid drops.

Research Task Description: The coalescence experiments are conducted in an immiscible acoustic levitator with degassed distilled water as the host medium. Silicon oil mixed with bromobenzene is the drop liquid. The mechanism involves levitating the first drop and then introducing the second drop. As the latter slowly seeks the same levitation position, the two drops come into contact with each other and coalesce. The coalescence is delayed until the host liquid between the drops is completely drained. The study of drops of large diameter ratios has been conducted in a vertical channel with water-glycerin mixtures of various viscosities as the drop liquid and silicone oil (DC 200, 100 cs) as the immiscible host through which a drop translates very slowly before coalescing with the bulk liquid at a flat interface.

For finite size ratio drops, the coalescence results in considerable mixing with the smaller drop penetrating the bigger drop as a vortex. The penetration of the smaller drops is basically dictated by the surface tension forces driving the motion, viscous drag resisting the motion, and diameter ratio of the drop. There is no mixing when drops are of equal size. For higher drop viscosity, the smaller drop is simply lodged in the larger drop, though by the same mechanism.

In order to quantify the mixing process, the case of very large size ratio of drops has been studied. Here the experimental results can be correlated with respect to the size of the smaller drop and the viscosity of the system. A water-glycerin system has been used as the drop liquid since the surface tension of the mixture is relatively invariant for the viscosity range (1-4 cP) studied. Drops of different sizes generated slowly translate through a viscous oil (DC 200, 100 cs) before coalescing at a flat interface. A laser induced fluorescence technique has been used to study the cross section of the flow field. Immediately following coalescence the drop enters the bulk fluid as a vortex that stretches and translates. Qualitatively this behavior is similar to that observed in finite size ratio drops. The mixing length (drop penetration) measured from the interface is the exponential distance the tip of the vortex translates before stopping.

The dependence of mixing length on drop viscosity is being examined at the current time. Efforts are being directed toward combining results for drops of different diameter ratios and explaining results observed in finite size ratio experiments.

Publications

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4. BIOTECHNOLOGY

Biosynthesis and Degradation of Cellulose under Microgravity Conditions

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Professor R. Malcolm Brown Jr.
NAG9-397
September 1, 1989 - May 31, 1991

Introduction: Cellulose is the most abundant macromolecule on earth. Some 10^{11} tons of this biobased material are made and destroyed each year. Cellulose consists glucose monomers linked β -1,4 glycosidically to form "glucan polymer chains". These chains associate laterally to form a highly crystalline submicroscopic rod known as the microfibril. At least two steps are involved in cellulose microfibril formation. First, a terminal enzyme complex generates the glucan chains, then these chains crystallize into a specific allomorph known as cellulose I (= native crystalline cellulose).

We are interested in understanding the processes of polymerization and crystallization leading to the formation of cellulose microfibrils. Because cellulose is assembled by living organisms which can sense gravity and respond by differential growth, it is of great interest to know how gravity affects this process. Because microgravity conditions are known to alter and promote crystallization patterns (example: protein crystal growth) of macromolecules, it becomes of interest to investigate how an enzymatically controlled polymerization reaction product may crystallize under microgravity conditions.

Objectives: The objectives of this research are: (a) to develop techniques to study native cellulose I microfibril assembly under microgravity conditions produced during parabolic flights of the KC-135 aircraft; (b) to use the gram negative bacterium, Acetobacter xylinum as one of the major test organisms, since it synthesizes crystalline cellulose in a time scale compatible with brief microgravity exposure on the aircraft; (c) to develop an understanding of any altered cellulose produced under these conditions; and (d) to apply ground-based gravity acceleration techniques with which to compare the microgravity-based data.

Research Task Description: The first microgravity experiment with Acetobacter was flown in the KC-135 aircraft in June, 1990. Further flights are planned for 1991. A video presentation covering this flight is available. For the in flight experiments, we developed a shock-mounted aluminum platform which provided a temperature-controlled environment for bacterial cellulose production. Seventeen Petri dishes were used to produce bacterial colonies on an agar surface three days before the scheduled flight. On agar, cellulose synthesis is limited, but can be induced by delivery of liquid culture medium to the agar surface. When flooded, the bacteria synthesize cellulose. Cellulose synthesis can be terminated by delivery of 50% ethanol as the fixative. Thus, the aluminum platform held the Petri dishes and associated nutrient and fixative delivery by syringes. An electronics package mounted on the pallet regulated temperature, monitored gravity, and counted parabolic cycles. Vital data were displayed with LCD and analogue metering. A continuous visual and aural record was made using a Hi-Band 8mm video camcorder mounted above the pallet.

The results of this first flight experiment were encouraging. We found that as Acetobacter synthesizes cellulose during progressive parabolic cycles, the cellulose ribbons become more disorganized. This disorganization is visualized in the form of separation of microfibril bundles from the compact ribbon. The ground and in flight controls had compact ribbons without splaying. At present, we cannot differentiate the cause for splaying. It may be due to successive 20 second exposures to microgravity or possibly the 20 seconds exposures to the 2x gravity during a parabolic cycle. To differentiate which part of the parabolic cycle is causal will require an additional series of experiments using time lapse video microscopy of bacterial cellulose ribbon assembly. With single frame analysis, it may be possible to accurately pinpoint when ribbon splaying is initiated. This is reasonable, since under conditions of splaying, the force for forward rotatable movement would be insufficient and thus, the bacterial motions would drastically change.

The first experiment will be repeated on at least two KC 135 flights in 1991, followed by video microscopy and in vitro synthesized cellulose crystallization studies. From a total of five planned flight experiments in 1991, we should have a better idea of the influence of brief periods of microgravity on biological polymerization and crystallization reactions. These data will be invaluable in correlating more complex metabolic and structural alterations which undoubtedly occur under microgravity conditions.

Crystallographic Studies of Proteins

Marshall Space Flight Center
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Dr. Xiao-min He
Pamela D. Twigg
Elena Casale
Jamie Walraven
Teresa Miller
In-House

Objectives: The objectives of this research are to: (1) determine and refine the structure of human serum albumin (HSA) to 3.0 angstroms resolution; (2) determine and refine the structure of a novel fungal lysozyme from *Chalaropsis*; (3) determine and refine the high resolution structures of the oxidized and reduced forms of cytochrome c5 from *Azotobacter*; (4) evaluate the effects of microgravity on the growth of selected protein crystals. In addition this laboratory will provide data collection opportunities to graduate students and researchers where such facilities are not available.

Research Task Description: Protein crystallography is currently the most powerful method for the determination of the three-dimensional structure of proteins and other macromolecules. This method usually requires crystals which are relatively large (0.5 mm - 1.0 mm) in size and possess a reasonably high degree of internal order. Consequently, protein crystal growth has become the subject of an increasing number of fundamental studies in crystal growth, including several ongoing microgravity experiments. The knowledge of the three-dimensional structure of macromolecules is of fundamental importance to the field of molecular biology, and it is presently receiving considerable attention from the biotechnology industry based on its promising potential for application in rational drug design and protein engineering.

We have constructed a diffraction laboratory for evaluating our results from ground-based experiments and our participation in flight experiments manifested on STS-26, STS-29, STS-31, STS-32. In addition to the evaluation of the x-ray diffraction properties of protein crystals, this laboratory is utilized to determine the three-dimensional structures of several challenging problems in molecular biology.

Crystals of several important proteins have been grown in our laboratory including a new crystal form of HSA, *Chalaropsis* lysozyme, cytochrome c5, the Fab portion of the antibody expressed against gp41 of the human immunodeficiency virus (HIV-I), and Interleukin 6. HSA is the most abundant protein of the circulatory system. There it plays several major roles in the transport, distribution, and metabolism of a diverse variety of endogenous and exogenous ligands. The three-dimensional structure of HSA was determined for the first time in our laboratory. The detailed atomic structure will provide a wealth of information regarding the many remarkable properties of this protein. *Chalaropsis* lysozyme is an enzyme which displays a broad spectrum bacteriolytic function and apparently belongs to a novel lysozyme structural class. A detailed understanding of the molecular structure will explain the chemical basis of the bacteriolytic function and could provide important information for future experiments in biotechnology. The crystals of cytochrome c5 diffract x-rays to very high resolution (approximately 1.0 angstrom) and will provide further insight into the mechanisms of electron transport. The structure of the HIV Fab will reveal important information concerning antibody/antigen interaction and offers additional insight into the design of new recombinant therapeutic antibodies. Interleukin 6 (IL-6) appears to be a key protein in the modulation of the immune system. Details of the IL-6 structure will provide important insights into the function of this extremely important cytokine. The structure determination and refinement of these and other protein crystals is actively in progress.

Progress to Date: The first year of funding has seen several major accomplishments. The three-dimensional structure of HSA was successfully phased to 4.0 angstroms using 21 heavy atom phase sets. The 4.0 angstrom structure, together with a variety of preliminary ligand binding experiments, has provided unprecedented insight into the structure and function of serum albumin. Numerous collaborations have developed with scientists around the world. Several crystallographic studies of related albumins, fragments of albumin, recombinant albumin, and albumins fetal counterpart alpha-fetoprotein are in progress. Higher resolution diffraction data were collected on imaging phosphors at the Photon Factory, a synchrotron source in Japan. The processing of this data should be completed in the near future. At this time, approximately 50% of the HSA structure has been fit with a polyalanine backbone. It is anticipated that the complete atomic model will be constructed and refinement of the coordinates initiated this year. Crystals of HSA and others were grown on shuttle flights experiments STS-26, STS-29, STS-31 and STS-32. The HSA crystals have revealed enhancements in quality similar to those previously reported by other co-investigators of the PCG flight experiments. Further investigations of the differences between ground-based and flight crystals will be addressed pending additional flight opportunities.

Preliminary 3.0 angstrom phases have been produced for the crystal structure of *Chalaropsis* lysozyme. The molecule appears to have a standard alpha/beta folding topology, thus describing novel structural class for the lysozyme enzyme family. Experimental work is continuing with the expectation of beginning the refinement of the 3.0 angstrom structure this year.

The high resolution refinement of cytochrome c5 based on the 2.5 angstrom structure is also beginning and is expected to proceed without complications.

An important accomplishment which was not included in the original proposal involves the recent crystallization and structure determination of the Fab portion of the antibody expressed against gp41 of the human immunodeficiency virus (AIDS). The antigen antibody complex has been successfully co-crystallized and shows diffraction to high resolution. The current atomic model has a standard crystallographic R-factor of approximately 19%. This will be the first report of a structure of an antibody and antibody/antigen complex to the AIDS virus. A manuscript describing these exciting results will be submitted to a major journal in the near future.

Small crystals of IL6 have been grown and efforts to improve the crystal growth conditions are in progress.

Overall this has been an extremely productive year and recent developments indicate that the upcoming year will our most productive thus far.

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Protein Crystal Growth in Low Gravity

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Robert C. DeMattei

Objectives: The ultimate objective of this research is the careful design of an experiment to study the effect of low gravity on the growth of protein crystals in a long-duration space flight. The proper design of the flight hardware and experimental protocols are highly dependent on understanding the factors which influence the nucleation and growth of crystals of biological macromolecules. Thus, the primary objective of this research is centered on investigating these factors and relating them to the body of knowledge which has been built up for "small molecule" crystallization. This data also provides a basis of comparison for the results obtained from low-g experiments.

Research Task Description: The main component of this research program is the study of mechanisms of protein crystal growth and those parameters which influence growth. Canavalin was chosen as a model protein to use in the studies. The program resolved itself into six tasks:

- 1) Solubility Studies - This research was designed to determine the solubility of canavalin and its dependence on temperature and solution parameters.
- 2) Growth Rate Studies - By studying the growth rate dependence of canavalin on supersaturation, the rate determining step of the growth process can be inferred.
- 3) Localized Supersaturation Control - Using the data from the solubility studies, methods of controlling local supersaturation in order to control nucleation events can be investigated.
- 4) Flow Imaging Studies - A study of the applicability of Schlieren imaging techniques to flows developed during protein crystal growth. In addition to canavalin, lysozyme and Rochelle salt will be used as models.
- 5) Protein Growth Model Development - Data gathered in this and other research will be used to develop a predictive model for protein crystal growth.
- 6) Space Flight Experiment - A conceptual design for a long-term space flight experiment will be developed.

Progress to Date: The growth behavior of isocitrate lyase was studied as a joint project with DuPont. The crystals grown by both DuPont and by CMR using the hanging drop method were "dendritic". Crystals grown in space as part of the DuPont program were more equi-axed. Similar crystals were grown at CMR in vapor diffusion cells which limited the surface area available for evaporation. Isocitrate lyase crystals grown in capillaries showed a "hexagonal" morphology. Diffraction studies (DuPont) of all three types of crystals show the same space group (orthorhombic) and only slight changes of the unit cell parameters. The changes in external morphology seem to be related to the rate of equilibration of the crystallizing solution.

A large scale mockup of the proposed space flight experiment has been built to test the ability to control the nucleation and growth phases of crystallization independently. The mockup consists of a temperature controlled chamber which holds the growth cell. The bottom of the cell has a temperature controlled spot (0.6 mm dia.) which is used to thermally induce nucleation. Temperature profiles taken with the spot at 10°C and the chamber at 25°C showed temperature gradients as high as 200°C/cm. This device (Thermonucleator) has been used to nucleate and grow crystals of ice, Rochelle salt and lysozyme.

Crystals of lysozyme have been grown using the temperature gradient method. This method utilizes the temperature dependence of solubility to transport material to the growth interface. The growth cell used for

these experiments was built on a microscope slide and had dimensions of 69.9 mm x 19.1 mm x 1.6 mm. Lysozyme powder was transported through a buffer solution from the hot end (25.5°C) to the cold end (15.5°C) of the cell where it deposited on a seed crystal. The initial growth rate was 0.56 μ /hr which dropped to 0.24 μ /hr when the crystal reached about 1050 μ in size. The crystal grew from an initial size of 780 μ to 1300 μ over a period of 1500 hrs. Oriented crystals of lysozyme and canavalin have been grown using artificial epitaxy (graphoepitaxy) for the first time. This technique uses a substrate patterned on a micron scale to induce orientation. In this study the pattern was a striated microrelief with a 5 μ + 5 μ period (groove depth was 2 μ) on silicon and oxidized silicon. In this technique, crystals are oriented by a combination of the interaction of crystallographic features with the edges of the grooves and by the capillary effect of the groove walls on small crystallites. The growth orientation observed did not depend on whether the crystals were grown on silicon or silicon dioxide which indicates that this is not true epitaxy. The patterned substrates also lowered the degree of supersaturation necessary for nucleation.

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Separation of Chromosomes-size DNA Molecules

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Dr. Young Cho, Drexel University
Dr. Lee Silver, Princeton University
NAG 8-748 (NASA Contact: R. Snyder, MSFC)

Objectives: This project addresses the problem of DNA separation by gel electrophoresis. Since we are interested in DNA molecules 10^6 - 10^8 base pairs in length (10^9 - 10^{11} daltons), or molecules that are polyanions of 2nm diameter with lengths of millimeters to many centimeters which distort as they move through the electrophoretic matrix, existing theories and models for electrophoretic transport processes must be modified.

Research Task Description: This effort will complement parallel national efforts to map and sequence the entire human genome. There are currently limitations in the human genome project which can be addressed by the technologies to be developed by this research project. Even if the human genome project is completed using existing methods, the technology to be developed here will extend the benefits of those efforts to all biological species, including those used as models of human disease and for agriculture and industry.

This project is an extension of NASA support of electrophoretic separation process development over the past decade. The extrapolation of currently employed methods for DNA separation suggests the use of more dilute electrophoretic media to allow larger porosity and consequently shorter reorientation times of the polymer subjected to pulsed electric fields. The only method to maintain fluid stability in the presence of chemical and physical density heterogeneity is the microgravity environment. Since the separated DNA will be used for genetic analysis, this program will keep space science applications at the cutting edge of biotechnology.

The investigations follow that outlined in the original proposal with emphasis on identifying the microgravity component. We have modeled the motion of DNA in Newtonian and non-Newtonian fluids using thin wire as a mechanical model. The results were unexpected and suggest the experiments for the next 12 months. The findings show that the wire falls end first, axis vertical, in the non-Newtonian fluid and longer wire falls faster. In the Newtonian fluid all wire lengths fall at the same rate, horizontally. This latter observation parallels the observations of Olivera, Blaine and Davidson [Biopolymers 2, 245-257 (1964)] where DNA of all length move at identical velocities in free Newtonian fluids in an electric field.

Construction of the apparatus to directly observe the orientation of DNA molecules during the electrophoretic process was completed in year 1. This instrument is in the laboratory at the Department of Chemistry, and initial experiments are suggestive of different degrees of DNA orientation in Newtonian compared to non-Newtonian fluids in an electric field.

Since our non-Newtonian fluid is a non-crosslinked polyacrylamide, the need for microgravity to prevent convection becomes obvious. Given the length of naturally occurring DNA, the dimensions of the electrophoresis system would need to be measured in meters rather than centimeters making Earth bound stabilization by density gradient less useful, if not useless. An absolute requirement for convection free fluid is necessary for resolution in the separation process. As an alternative matrix for the DNA process, glass bead material described in the original proposal was explored. Experiments are in progress to establish that megabase lengths of DNA are indeed electrophoresed gels in the presence of glass beads of 170-200 μ diameters.

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Protein Crystal Nucleation

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In-House

Objectives: The objectives are a comprehensive understanding of the nucleation and crystal growth processes for biological macromolecules by using standard technologies such as light scattering, protein-protein cross-linking, and isothermal calorimetry. Areas of specific interest currently center on the mechanisms of protein desolubilization when bound by precipitating molecules and the early steps in the pathway by which soluble monomeric protein molecules become insoluble aggregates. Elucidation of the macromolecular assemblies present in solution are also important for understanding of the data obtained in crystal face growth rate experiments also in progress in this laboratory, and in determining the role that microgravity may play in improving the protein crystal growth process.

Research Task Description: A multi-angle light scattering apparatus has been assembled for use in aggregation studies. Concurrently, a rapid kinetics apparatus has been obtained and connected to the older 90° light scattering/fluorescence apparatus for use in measuring the early kinetics of the nucleation process. Several micro-solubility apparatus's, originally designed in this laboratory, have been delivered and are all currently being used for determination of various protein solubilities.

Nucleation is a complicated process which is not very well understood, even for small molecules. With proteins, we have an opportunity to study this process in systems with which we have quite a bit more experimental access to the nucleating molecules. Light scattering, difficult with small molecules, is relatively easy with proteins. Most proteins have at least one fluorescent amino acid and if not, or if unsuitable, specific fluorescent probes may be attached for following local changes about the protein molecules as they assemble into nuclei. Protein molecules can be cross-linked while still retaining their function, which can also be exploited in nucleation studies. The approach taken by this laboratory is designed to exploit these strengths of protein-based systems. Initial experimental work has done using the hen egg white protein lysozyme, a well characterized and easily crystallized material. Recently, we have begun to branch out to other proteins of interest.

Progress to Date: As knowledge of the solubility behavior is fundamental to any study of the solution behavior of a solute, initial efforts were concentrated on obtaining a lysozyme solubility diagram. Completion of the first part of this diagram for the tetragonal form has now been completed, covering the solubilities from pH 4.0 to 5.4, 2.0 to 7.0 %NaCl, and 4.0 to 25°C. In all instances the solubilities were found to be normal, i.e., increasing with increasing temperature, and decreasing with increasing salt concentration. The solubilities are found to decrease with increasing pH at low salt concentrations, but increase with increasing pH at high salt concentrations. Calculated thermodynamic parameters using the Van't Hoff equation show the lowest values for dH and dS are at low pH and salt concentrations. With completion of this part of the lysozyme solubility diagram, work has been initiated on the corresponding portion of the orthorhombic solubility diagram (temperatures > 25°C and on the solubility diagrams for the proteins alpha-Chymotrypsinogen-A (which has retrograde solubilities) and Concanavalin A. Both proteins are crystallized under similar conditions using ammonium sulfate at neutral pH.

Light scattering kinetic studies of the nucleation process for lysozyme has shown a critical dependence upon the salt concentration. At 0.375 M NaCl, 20°C a 7.5 mg/ml solution has virtually

no aggregation. However, at 0.5 M NaCl, same conditions, rapid aggregation is observed. Other aspects of the aggregation process have been observed while following the Cl⁻ ion concentrations. Current experimental results indicate that Cl⁻ is very rapidly bound by the protein prior to any aggregation. However, during aggregation some of the bound Cl⁻ ion is released back into the solution. This then increases the free Cl⁻ concentration, resulting in more being bound to the still soluble protein, causing increased aggregation, etc., somewhat complicating how one defines the equilibrium conditions of this system. Experiments using equilibrium dialysis have been initiated to begin investigating this problem.

Cross-linking studies using glutaraldehyde have been done in an effort to elucidate the aggregation pathway. So far, no isolated cross-linked material has been found to clearly give crystals, although some have shown what appears to be microcrystalline precipitates. One problem with using lysozyme in these experiments is that it is typically crystallized at acidic pH's, which is not a suitable range for the available cross-linking agents. This is one of the reasons why we have initiated solubility diagram determinations for other proteins, which may in future prove to be more suitable subjects for these experiments .

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Nucleation and Growth Control in Protein Crystallization

University of Alabama in Huntsville
Center for Microgravity and Materials Research
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Dr. Edward Meehan
Dr. Thomas Nyce
NAG8- 711 (NASA Contact: R.S. Snyder, MSFC)
March 1988 - March 1990

Objectives: The inability to routinely grow crystals of sufficient size and quality for diffraction is considered the major bottleneck in the further widespread development of the field of protein crystallography. By comparison with inorganic crystal growth, the fundamental understanding of the dynamics and kinetics of protein crystallization is still rather rudimentary. Correspondingly, the existing protein crystal growth technology provides only for limited control of essential growth parameters such as supersaturation and, consequently, the number and timing of nucleation events, and the growth rate. Most protein growth experiments to-date result in a large number of small crystals. In low gravity growth experiments these uncontrolled growth conditions can become somewhat mitigated. The reduction of buoyancy-driven, solutal convection reduces the probability for concurrent nucleation in the vicinity of initially formed crystallites. This may be one of the reasons for the increase in size and decrease in the number of protein crystals that have been obtained in space.

The objectives of this research program are: (a) the determination of the advantages and drawbacks of using temperature as the control parameter in protein growth; and (b) the development of a semi-automated protein crystal growth technology that excludes further nucleation after select initial nucleation or seeding, and provides for the controlled, non-interfering growth of the initial nuclei or seeds; and (c) contributions to the understanding of the dynamics and kinetics of protein crystallization in general.

Research Task Description: Towards these objectives we have: (a) developed a technique for the expedient, semi-automated determination of protein solubilities as a function of temperature, and application to other proteins than lysozyme; (b) developed a small solution cell for the growth of (individual) protein crystals at a predetermined location through temperature programming; (c) developed a microscopy system with image storage and processing capabilities for high resolution (interferometric) studies of protein growth and etching kinetics; (d) concluded the growth experiments with lysozyme in a thermosyphon flow arrangement that were begun under NASA Grant NAG8-098; and (e) developed a mathematical model for the evolution of evaporation/diffusion-induced concentration gradients in the hanging drop protein crystallization technique.

Progress to Date: Progress has been excellent. We have been able to show that the temperature dependence of protein solubilities can readily and accurately be determined for small volumes of solution with a scintillation (light scattering) technique. Solubility data have been determined semi-automatically for lysozyme, canavalin and horse serum albumin, with the latter showing pronounced retrograde solubility. These data have been advantageously used for the control of nucleation and growth of protein crystals through temperature variations. Specifically, we have succeeded in growing lysozyme and horse serum albumin single crystals of sufficient size inside glass capillaries used for x-ray diffraction studies.

For the high resolution growth and etching kinetics studies we have built a novel thermostated solution cell that permits the in-situ monitoring of crystal surface morphologies by differential interference contrast transmission and interferometric microscopy. In connection with an image storage and processing system with 1024x1024 lines resolution, a depth resolution of a few hundreds Å can be achieved. Preliminary results obtained with lysozyme reveal that significant defect concentrations can result upon temperature changes of 1°C

during growth. It should be noted that these defects, which likely consist of irregular inclusion of mother liquor into the crystal, cannot be observed with standard reflected light microscopy and without image processing.

Furthermore, we have shown that forced convective flows can be detrimental to protein crystal growth. Specifically, in experiments with lysozyme crystals suspended in a thermosyphon flow, we found that tetragonal lysozyme did not grow beyond 0.1 mm in size, even under supersaturations that caused continuous nucleation in the solution. Microscopic examination revealed that these crystals lacked well defined facets. Yet, when transferred to a stagnant control solution, the crystals showed uninhibited growth. Orthorhombic lysozyme crystals, on the other hand, did not exhibit a growth cessation in the forced flow.

In addition, the thermosyphon experiments gave some insight essential for the development of seeding techniques. We found, for instance, that if a tetragonal lysozyme seed experiences a temperature change of several degrees during transfer to a supersaturated solution, it will not grow thereafter. Furthermore, when the solution into which a seed was transferred differed in salt concentration by as little as 0.003 g/ml, no growth occurred. Hence, before seed transfer, special measures have to be taken to assure continued growth of a seed.

The transport model calculations for the hanging drop technique have shown that, depending on the diffusivity (i.e. size) of the protein involved, significant protein concentration gradients can develop in the drop under purely diffusive conditions, whereas the drop will remain well mixed with respect to the salt concentration.

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Electrophoresis Technology

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In-House

Objectives: The objectives of this program are to: (1) analyze the fluid flow and particle motions during continuous flow electrophoresis by experimentation and computation; (2) characterize and optimize electrophoretic separators and their operational parameters; (3) develop innovative methods to accomplish electrophoretic separations in space; and (4) analyze the electrophoretic process using apparatus that has been characterized or modified to perform in a predictable manner and according to procedures that have been developed to yield improved separation.

Research Task Description: Both horizontal and vertical laboratory electrophoresis test chambers have been built to test the basic premise of continuous flow electrophoresis that removal of buoyancy-induced thermal convection caused by axial and lateral temperature gradients will result in improved performance of these instruments in space. These gravity dependent phenomena disturb the rectilinear flow in the separation chamber when high voltage gradients and/or thick chambers are used, but distortion of the injected sample stream due to electrohydrodynamic effects causes major broadening of the separated bands observed in these chambers.

The electrophoresis separation process can be considered to be simple in concept but flows local to the sample filament produced by the applied electric field have not been considered. These electrohydrodynamical flows, formulated by G.I. Taylor in 1965 for drops suspended in various liquids, distort the sample stream and limit the separation. In addition, electroosmosis and viscous flow, which are inherent in the continuous flow electrophoresis device, combine to further disturb the process. Electroosmosis causes a flow in the chamber cross section which directly distorts the sample stream, while viscous flow causes a parabolic profile to develop in the flow plane. These flows distort the electrophoretic migration of sample by causing a varying residence time across the thickness of the chamber. Thus, sample constituents at the center plane will be in the electric field a different length of time and hence move more or less than comparable constituents closer to the chamber wall.

A moving wall concept has been developed for laboratory testing which will eliminate and/or control all of the above-mentioned disturbances. The moving wall will entrain the fluid to move as a rigid body and hence produce a constant residence time for all sample distributed across the chamber thickness. By aligning the moving wall at an angle to the chamber axis, a component of the moving wall motion can be made to oppose and hence cancel the electroosmotic flow. In the absence of electrokinetic effects, i.e. electroosmosis, the electrohydrodynamical effect manifests itself as a ribbon, being either vertical (perpendicular to the electric field) or horizontal (aligned with the electric field) depending on the ratio of conductivity of the sample to that of the buffer. Therefore, by using low conductivity sample solutions to provide a vertical ribbon, the moving wall concept should produce distortion-free separations.

A new electrophoresis-type test chamber has been built and put into operation. This chamber has the feature of two dimensional observation of the sample stream as well as observation of the sample stream cross section. The cross section is observed by means of a cross section illuminator which assures that the sample stream distortion can be accurately recorded.

Chamber wall zeta potential control is important in all types of electrophoretic separations. Experiments are currently underway to evaluate a published method to control electroosmosis by using an external electric field. Several test chambers have been built to evaluate this control process in glass capillary tubes.

The separation of intact, chromosome-size DNA molecules is necessary to map and sequence the entire human genome. A method to accomplish this is being investigated using free fluid electrophoresis. A very high magnification microscope along with an associated test chamber is being set up to determine the orientation characteristics of DNA molecules under the influence of an AC electric field.

Progress to Date: Through analysis and experiments, we have found that sample stream distortion is initiated by variations in conductivity and dielectric constant between the sample stream and the buffer medium. While the effect of conductivity variations is clearly understood, the dielectric behavior of colloidal suspensions which make up the sample stream is not at all clear. Indeed, a large discrepancy exists between the published experimental dielectric data and classical theory.

Preliminary results show that the electronic zeta potential control is very sensitive to the cleanliness and or the surface conditions of the glass capillary. Further tests are planned to determine the exact mechanism of the zeta potential modification by the electric field. Also, coatings will be tried in an attempt to make the electronic zeta potential control less sensitive to wall surface conditions.

A method to experimentally determine the dielectric constant of colloidal suspensions by observing the distortion of sample streams has been investigated. Sedimentation of the large sample concentrations needed to perform the experiments precluded the development of meaningful correlation between sample stream distortion and dielectric constant. These studies will have a direct influence on the understanding of sample stream distortion in continuous flow electrophoresis.

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Growth of DNA Crystals in a Microgravity Environment

University of Pennsylvania

Donald Voet

J. LaLonde

NAG8-770 (NASA Contact: K. D. Sowell, MSFC)

July, 1989- June, 1991

Objectives: The objective of the research is to determine the X-ray structure of several large segments of double stranded DNA. To this end it is necessary to crystallize the DNA. Since DNA is difficult to crystallize in a form suitable for X-ray diffraction, we are proposing to study the effects of microgravity on DNA crystallization.

Research Task Description: We intend to synthesize and crystallize several non-self complementary segments of B-DNA in the range 12-20 base pairs. The crystals, when obtained, will be used to determine the X-ray structure of the DNA's in order to establish how the DNA conformation varies with its base sequence.

Progress to Date: We have synthesized seven different species of non-self-complementary double stranded DNA ranging in size from 12-20 base pairs. We have developed new methods of purifying these substances and have crystallized three of them: (1) a 12-base pair segment which may be suitable for X-ray analysis; (2) a 20-base pair segment which yet too small for X-ray analysis but which we are hopeful of growing larger, and (3) an 18-base pair segment. The 12-base pair segment was tested for crystallization under microgravity on STS-32. Unfortunately, the refrigerator cooling the experiment did not work during the first day of the experiment. Consequently, only showers of microcrystals were observed (the DNA does not form suitable crystals at room temperature on the ground). We have since synthesized, purified and crystallized several other double-stranded DNA's. Some of them are favorable candidates for microgravity crystallization.

5. GLASSES AND CERAMICS

Use of Microgravity to Improve the Efficiency and Power Output of Ni-Doped Laser Glasses

University of Missouri-Rolla

Dr. Chandra S. Ray

NAG8-779 (NASA Contact: E. Ethridge, MSFC)

July 1, 1989 - June 30, 1991

Objectives: The efficiency and power output of Nd:glass laser increases initially with increasing concentration of Nd^{3+} ions in the host glass and then decreases after a critical concentration is reached. This effect, known as concentration quenching, occurs when the mean separation between two neighboring Nd-ions becomes less than a critical value d_c , and sets an upper limit to the Nd-ion concentration in a laser glass. At a mean ion separation, $d < d_c$, the effect of ion-ion interaction which decreases the ratio for radiative to nonradiative transitions, becomes important and deteriorates the overall laser properties of the glass. The presence of impurities in the glass also causes a similar effect which is called impurity quenching.

Glasses prepared on earth are reported to contain microheterogeneous regions which can cause the mean ion separation in a laser glass to reach the critical value, d_c , at Nd-ion concentration much less than what is needed to reach d_c when the ions are homogeneously distributed. Glasses prepared in microgravity are reported to be more chemically homogeneous and to contain fewer impurities than glasses prepared on earth. The major objectives of this investigation are to, therefore:

- 1) increase the concentration of Nd^{3+} ions in various glasses prepared in microgravity before concentrations quenching becomes important, thereby, preparing laser glasses with increased output power per unit volume,
- 2) decrease the threshold energy (minimum energy required to start laser action) and further increase the output power by suppressing or eliminating impurity quenching in glasses processed without container,
- 3) compare selected properties such as fluorescence efficiency (ratio of input to output energy), fluorescence lifetime and bandwidth, and crystallization kinetics for the laser glasses prepared in microgravity and on earth.

The anticipated results from this study will provide quantitative data showing the extent to which the power efficiency is increased and the threshold energy is decreased for laser glasses prepared in microgravity. The practical use would be to take advantage of the higher compositional homogeneity and chemical purity for glasses prepared in microgravity to produce laser glasses that would yield more output power per unit volume than the glasses melted on earth.

Progress to Date: Laser glasses in the silicate and phosphate systems have been prepared with different Nd_2O_3 concentration. The lifetime of the fluorescence of 1060 nm ($4F_{3/2} \rightarrow 4I_{11/12}$ of Nd^{3+}) for these glasses have been measured using an apparatus constructed by ourselves. A technique based on the Judd-Ofelt theory has been developed to measure limit for concentration quenching from absorption measurements, which appears particularly suitable for smaller size samples (<4 mm diameter). The limits for concentration quenching measured by this method for the silicate and phosphate laser glasses are in excellent agreement with those reported with others. Selected other properties such as refractive index, density, chemical durability for these glasses have also been measured as a function of Nd_2O_3 concentration. Samples containing different amounts of Nd_2O_3 in these silicate and phosphate systems and suitable for containerless processing in the high temperature acoustic levitation isothermal furnace (ALF) now being prepared.

Presentations

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Glass Formation and Crystallization Behavior

University of Arizona
Dr. Michael C. Weinberg
Dr. George F. Neilson

Objectives: The objectives of this program are the analysis of the crystallization behavior of marginal glass-forming systems (with the goal of assessing the possibility of containerless experiments), the experimental investigation of the crystal nucleation and growth of simple, model glasses, and the theoretical interpretation of experiments used to determine nucleation and crystallization rates.

Research Description: Crystal nucleation may be enhanced by the presence of foreign substances in contact with the melt. Since crucible walls and contaminants introduced into the melt from the crucible can serve as heterogeneous nucleation sites, an uncontained melt might be subject to homogeneous nucleating conditions. However, in order to assess the potential advantages of containerless processing at least two items are needed: (1) comparative ground based nucleation and crystallization data, (2) a more comprehensive knowledge of the factors which influence the crystallization behavior of glasses and reliable theory to explain and interpret such ground based experiments. It is the purpose of this program to address some of these issues which allow for judicious choices of glasses for flight experiments and enable one to interpret their results.

Progress to Date: We have provided theoretical analysis of certain aspects of the standard description of thermoanalytical crystallization experiments. In particular, the applicability of the assumption of an Arrhenian temperature dependence of the crystallization rate constant has been assessed for certain non-isothermal transformations. Also, we have compared the glass-forming ability of a calcium niobate composition prepared by conventional and sol-gel methods. This composition was identified as a potential candidate by Ralph Happe many years ago. Finally, we examined two aspects of heterogeneous crystallization. The results of these studies could help evaluate the impact of heterogeneous crystallization and allow for its quantitative determination.

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6. COMBUSTION SCIENCE

The Combustion of Free of Unsupported Fuel Droplets at Low Gravity

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NAG3-987 (NASA Contact: J. Haggard, LeRC)
October 1989 - October 1990

Objectives: The objective of this work is to study experimentally the combustion of small unsupported and isolated fuel droplets within a low gravity environment. The experimental method attempts to create a fundamental configuration for the droplet combustion process, namely near spherically symmetric combustion. In this way, the data obtained may be applied to model development in which spherically symmetric combustion has been assumed. Accounting for asymmetries in droplet combustion which are induced by a significant axial vapor flow around the droplet can complicate model development, especially if it is desired to also model other aspects of the droplet burning process such as extinction and soot formation. The emphasis in the experiments has been to examine the burning characteristics of multicomponent droplets, especially droplets which are miscible mixtures of liquids. Thus far, binary droplet systems have been studied.

Research Task Description: A low gravity environment is created by performing the experiments within a drop tower. The test droplet, its surrounding combustion gases (room temperature air in the present experiments), and associated optical equipment (to record the droplet burning process) are simultaneously released into free-fall. The droplet then experiences a low gravity environment within the moving frame of reference. The photographic results provide information about the occurrence of such phenomena as extinction, microexplosions, and soot formation. The droplets are small enough (nominally with an initial diameter of about 500 μm) that their complete combustion history can be recorded within the available experimental time.

Progress to Date: Progress was made over the past year on both apparatus development and experimentation.

Modifications to the apparatus which were made over the past year included: (1) allowing for ignition of the droplet after the period of free fall (i.e. low gravity) began, (2) using two electrode pairs symmetrically placed around the droplet to ignite the droplet; and (3) constructing an electrode mount which allowed the electrodes to be retracted after ignition. The mixture components were selected to study the effect of additives on soot formation, burning rate, microexplosions, and extinction.

A matrix of tests are completed which examined the burning characteristics of mixtures of methanol and dodecanol. The propensity for this mixture to experience microexplosions is not effected by the presence of soot because both components in the mixture produce little soot during combustion. Microexplosions may then be initiated by homogeneous nucleation within the burning droplet. A range of methanol compositions was observed over which microexplosions occurred. The process characterized by a bubble growing within the droplet which produced a balloon-like sphere which then burst and created several fragments. Also, an extinction-like phenomenon was consistently observed for methanol but not for mixtures of methanol and dodecanol for the compositions studied.

Experiments were also initiated over the past year to examine the control of soot produced by burning a highly sooting liquid. Binary mixtures of toluene and methanol, and heptane and a chlorinated hydrocarbon, were studied for this purpose. The results provided observations of the development of the spherical soot shell structure around the droplet, and the influence of composition on soot formation. Methanol/toluene mixtures revealed a dramatic influence of methanol on soot formation. When burned

alone, toluene soots extensively. However when a toluene droplet was sufficiently diluted by methanol, the experimental results showed that the mixture droplet burned without producing observable soot - the soot shell that characteristically forms during combustion of toluene droplets was not observed for certain concentrations of methanol and toluene. Extinction was observed for all methanol concentrations studied. A limited set of experiments using fiber supported droplets was also carried out to examine the combustion of mixtures of heptane and chloro-octane. The heptane/chloro-octane is an example of a mixture for which both components produce soot, though heptane less so than chloro-octane. The nominal initial droplet diameters in the suspended droplet studies were about 1000 μm . The results revealed a less dramatic effect of composition on soot formation.

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Particle Cloud Combustion

University of California, San Diego

Professor A. L. Berlad

Dr. K. Seshadri

Dr. V. Tangirala

NAG3-925 (NASA Contact: H. Ross, LeRC)

Objectives: The principal objectives of this microgravity experimental program are to obtain flame propagation rate and flame extinction limit data for several important premixed, quiescent particle cloud combustion systems under near zero-gravity conditions. The data resulting from these experiments are needed for utilization with flame propagation and extinction theory. These data are also expected to provide new standards for the evaluation of fire hazards in particle suspensions in both Earth-based and space-based applications. Both terrestrial and space-based fire safety criteria require the identification of the critical concentrations of particulate fuels and inerts at the flame extinction conditions. Recent findings encourage the broadening of these objectives to include studies of both uniform and nonuniform particle cloud systems.

Research Task Description: The Particle Cloud Combustion Experiment employs long flame tubes within each of which a uniform quiescent cloud of particles is to be suspended in reduced gravity. Particulates under study include the fuels Iycopodium, cellulose and coal, as well as a number of inert particulates. Systems of additional interest include initially uniform clouds of inert particulates in premixed combustible gases. Ground-based supportive studies include the use of the LeRC drop tower and Learjet research facilities as well as the laboratories at the University of California, San Diego. Laboratory experiments include studies of particle cloud mixing, particle-particle interactions, pyrolysis-vaporization kinetics, and the radiative attenuation properties of individual particles and of particle clouds. LeRC drop tower and Learjet facilities are employed to study particle cloud mixing and particle cloud combustion phenomena in reduced gravity.

Progress to Date: LeRC drop tower and Learjet facilities have been used successfully to study lowgravity particle mixing and flame propagation phenomena supported by quiescent clouds of lycopodium particulates. These studies also include clouds of brown coal, with and without inert particulates. One mode of quasisteady flame propagation observed involves a well behaved flame front whose transport is radiatively driven. Theoretical relations between these observations and those for our previously observed stabilized Iycopodiumair flames have been developed. Additionally, a strikingly novel mode of flame propagation has been observed and analyzed. These latter flames are called *Chattering Flames* and result from flame-induced acoustic excitation of the Kundt's Tube phenomenon. This leads to spatial segregation of the fuel particles into regularly arranged laminae. Flame-induced acoustic segregation of particulates implies important safety-related consequences for systems of combustible particulates in reduced gravity as well as in normal gravity. Theoretical analyses have been conducted for *Chattering Flames* as well as for the more normal flame propagation mode. Analyses have been enlarged to include those for nonuniform concentrations of particulates as well as for clouds of inert particulates in premixed gaseous fuel plus oxidizer.

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Scientific Support for a Proposed Space Shuttle Droplet Burning Experiment

Princeton University

Professor Frederick L. Dryer

NAS3-24640 (NASA Contract: Mr. John B. Haggard, Jr., LeRC)

May 1985 - December 31, 1990

Joint Research with University of California, San Diego, Professor Forman A. Williams

Objectives: The general objective of this program is to ascertain how best to utilize reduced gravity facilities to pursue scientific investigations of droplet combustion. The scientific investigations of droplet combustion. The scientific objective is to provide scientific support for development of a droplet combustion experiment module for conducting experiments in the NASA LeRC microgravity facilities, and possibly aboard a space-based platform such as the Space Shuttle or in the Space Station. The planned experiments are intended to improve fundamental understanding of droplet combustion phenomena, especially in relationship to time-dependent characteristics and extinction phenomena. the scientific-support objective encompasses data acquisition and reduction as well as asymptotic and numerical modeling for interpretation of observations.

Research Task Description: The research tasks include theoretical modeling using asymptotic and numerical techniques, with emphasis on transient phenomena, detailed chemical kinetics and transport effects, ground-based experimentation on droplet burning in both the 2.2 and 5.5 second NASA LeRC drop towers, support to NASA in providing advice on hardware aspects of a flight experiment and a analysis of data to be obtained from all experiments. The modeling addresses questions related to transient burning, to soot formation and destruction, to droplet disruption, and to ignition and extinction phenomena. Ground-based experiments have been focused on droplet ignition and on impulses imparted to droplets by ignition sparks; spark designs for minimum impulse were addressed. In addition, drop-tower experiments are addressing burning-rate measurements and mechanisms of soot production and of droplet disruption, as well as extinction phenomena. Work has encompassed n-decane, n-heptane, and methanol as fuels in oxidizer/inert mixtures at pressures between about 0.2 and 2 atmospheres.

Progress to Date: In this work we have obtained data on the spherically symmetric burning of decane, heptane and methanol droplets in a range of ambient environments. The importance of the interaction between the spark and the droplet in the ignition of the a droplet was established. Also, the importance of soot formation and how it influences the burning characteristics of hydrocarbon fuel droplets were demonstrated. Disruptive phenomena in droplet combustion were recorded and explained. The development of methods to employ a digital data processing technique for analyzing droplet combustion data was completed, and this was applied to droplet-burning data from drop towers. Identification of product dissolution in the liquid phase of a droplet was made, and clarification of histories of impurity buildup in the liquid during droplet combustion was achieved. Identification of a new 'slow' burning regime for hydrocarbon fuel droplets resulted from this joint research. In recent experiments it was found that the oxygen index limit for droplet combustion in microgravity is lower than in normal gravity.

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A Fundamental Study of the Effect of Buoyancy on the Stability of Premixed Laminar Flames

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Objectives: The objective of this research is to investigate the effect of buoyancy on the stability of premixed laminar flames. The information obtained will help in the understanding of the mechanisms responsible for instabilities in laminar flames which are often regarded as precursors of turbulent combustion processes. The immediate objective is to perform a set of low-gravity, ambient pressure drop tower experiments to elucidate the effect of the absence of gravity on the onset and evolution of cellular flame structure.

Research Task Description: The research task consists of the experimental determination of the gravity effect on the stability and cellular structure of premixed flames both anchored on a porous burner and propagating through a tube. Low-gravity, atmospheric pressure tests are performed in the NASA LeRC 2.2-sec Drop Tower. The resulting flame images for the normal and microgravity tests are compared to observe, through the cellular structure, the effect of gravity on the flame stability. These experiments are complemented with a similar series of tests performed at varied ambient pressure. Since the ambient pressure affects the buoyancy force, diffusivity and reaction rate, comparisons of the different results are used to determine the importance of gravity with respect to other mechanisms in the overall flame stability.

Progress to Date: Microgravity experiments have been conducted in the NASA LeRC 2.2-sec Drop Tower to investigate the effect of buoyancy on the stability and structure of cellular premixed propane-oxygen-nitrogen flames. Tests have been carried out at both normal and microgravity conditions, for several configurations. These include upwardly- and downwardly-propagating flames anchored on a cooled porous-plug burner as well as propagating in a vertical tube. The former configuration offers a convenient way to study these flames, yielding cells with very regular shapes and sizes. The latter configuration largely eliminates the effect of heat loss, which has been found to exert an important stabilizing influence on burner flames. Flame characteristics were recorded on high-speed film, and normal-gravity flames have been compared to those in low gravity. Differences in flame structure are interpreted in terms of the expected effects of buoyancy.

1. Burner Flame Experiments

Initial microgravity experiments with burner-anchored cellular flames propagating downward were performed in FY 89. Those tests showed little change in flame characteristics in the absence of gravity for most of the conditions throughout the cellular regime. Lifted flames just outside the Rich Cell Limit, however, were observed to become cellular when gravity was reduced. A paper reporting this work has been presented at the 1989 Fall Technical Meeting, WSS/CI.

Further experiments in this configuration over a broader range of flow conditions have been carried out in FY 90. A paper reporting this work has been presented at the 23rd Symposium (International) on Combustion. In addition, normal and low-gravity studies were conducted of burner-anchored cellular flames propagating upward. Results show that in normal gravity conditions, the range of mixture conditions for which the cellular instability appears is broader for upwardly-propagating flames than for downwardly-propagating flames. At a given flow rate, the mixture composition at which a planar flame begins to show cellular structure (the Lean Cell Limit) is slightly leaner for the upwardly-propagating flames. In addition, the composition at which the cellular flame becomes lifted (the Rich Cell Limit) is significantly richer when

the flame propagates upward. Hence, the band of rich propane-oxygen-nitrogen mixtures for which cells occur is wider for upwardly-propagating flames.

In microgravity, the Lean Cell Limit (LCL) appears unchanged for flames propagating downward. For the upwardly-propagating configuration, however, 1-g cellular flames in mixtures slightly richer than the LCL become planar in μg . This confirms that the microgravity LCL does not depend on the direction of propagation. Near the Rich Cell Limit (RCL), downwardly-propagating flames that are lifted in normal gravity become cellular in reduced gravity. Upwardly-propagating flames at the same mixture conditions, however, are cellular in 1-g but become lifted and distorted cells in μg . This indicates that the low-gravity RCL is also independent of propagation direction, and occurs for a mixture intermediate between the normal-gravity RCLs for the upwardly- and downwardly-propagating flames.

These observations are consistent with the expected stabilizing or destabilizing effect of buoyancy, which depends on the direction of flame propagation. However, one must exercise caution in interpreting these results to strictly reflect the intrinsic role of buoyancy in the flame stability. Many of the observed differences in flame structure between the various g-levels (1-g upward, 1-g downward, low-g) can be explained instead by changes in the flow field surrounding the premixed flames, along with the increase (decrease) in the flame propagation speed in low gravity for flames propagating downward (upward). Selected images of burner flames in the various g-levels have been assembled in composite photographs, and are currently being readied for publication.

2. Tube Flame Experiments

To eliminate the effects of interaction between the flame and the burner surface, normal and low-gravity experiments have also been conducted with flames propagating in a tube. In these tests, combustible mixture emerges from the porous burner and enters a vertical tube of the same diameter. The mixture is ignited at the opposite end of the tube, and the flame propagates toward the burner, against the flow of fresh gas.

These flames are found to exhibit more dramatic behavior in low gravity than that previously observed for burner flames. Downwardly-propagating flames that are *planar* in 1-g become curved toward the unburned mixture in low g, forming a single cell nearly filling the tube. This behavior is consistent with theoretical predictions that flat flames are possible only when the stabilizing effect of buoyancy in this geometry counters the so-called hydrodynamic instability mechanism. Thus when gravity is reduced, the hydrodynamic instability is unopposed and produces a curved flame.

Behavior of cellular tube flames is considerably more complex. Mixtures producing small cells in downwardly-propagating flames are found to produce a smooth bubble-shaped flame in upward propagation, which breaks into small, regular cells when nearing the burner. In reduced gravity, these mixtures produce flames with larger, irregular cells. Often, one cell grows at the expense of the others, which rise and disappear. The remaining cell propagates through the tube as an oblique curved flame, while smaller cells form and disappear along its surface.

These observations are interpreted qualitatively in terms of the predicted effects of buoyancy on flame stability and cell sizes. It is concluded that while buoyancy is not the dominant mechanism producing cells in these flames, it contributes significantly to the overall flame stability and structure. Comparisons of microgravity burner and tube flames indicate that previous microgravity observations of burner flames showed little change from normal-gravity cellular structure because the presence of the burner overwhelms the effects of buoyancy. Selected images of tube flames in the various g-levels have been assembled in composite photographs, and are currently being readied for publication.

Publications

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A Fundamental Study of Smoldering with Emphasis on Experimental Design for Zero-G

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NAG-3-443

Objectives: The objective of the overall research program is the design and performance of smolder combustion experiments under microgravity conditions, to help understand the mechanisms controlling smoldering, and in turn the prevention and control of smolder originated fires in normal gravity and in space-based environments. The specific objectives are: to develop ground-based experiments to determine the effect of gravity on the different modes of smoldering; to perform drop-tower tests to obtain data on the smolder transition processes of ignition, flaming and extinction; and to use these data to design a space-based smoldering combustion experiment.

Research Task Description: The current research program is primarily experimental. Experiments are being conducted to determine the range of conditions for which smolder is affected by gravity, and how gravity affects the smolder process and its transition to flaming. The approach being followed is to measure the smolder velocity through materials of varied void fraction as a function of the velocity of a mixed (free and forced) oxidizer flow, for both downward and upward propagation. Comparison of the measurements for the two geometrical configurations allows the determination of the conditions where gravity affects smoldering. This information is then used toward the design of the space-based experiment.

The smolder process is too slow to obtain significant microgravity information in droptower, or parabolic flight experiments. However, such experiments can provide information about the microgravity behavior of the transition processes of smolder ignition, flaming and extinction. With this objective in mind, the present research task includes a series of droptower tests aimed to obtain information about the suitability of the different ignition methods to initiate the smolder process in a microgravity environment.

Progress to Date:

1) Normal Gravity Experiments

A series of experiments in normal gravity for downward and upward, natural convection, opposed flow smoldering of polyurethane foam have been completed. The experiments show that buoyancy can only induce a flow of oxidizer through the porous combustible if its thickness is relatively small (5 cm. in the present case), but that the air contained in the foam pores may be sufficient to sustain smolder. Under these conditions the smolder velocity for both upward and downward smolder are similar. This result could be of particular importance if smoldering were to occur in a spacecraft, since microgravity provides an insulating environment and the heat from the smolder reaction, not being removed, could lead to a transition to flaming. A paper reporting this work has been presented at the 1990 Spring Technical Meeting, WSS/CI.

A second series of experiments has been conducted and is almost completed to study mixed, free and forced, opposed flow smoldering, with the objective of determining the range of flow velocities at which buoyancy has a significant role in the process. This is accomplished by comparing the results for upward

and downward smoldering. The results show that the smolder velocity attains a maximum at flow velocities of approximately 2.5 mm/sec, and that buoyancy plays a role in the smolder process in the last 5 cm of the sample. The analysis of the results confirms that the smolder process is controlled by the competition between the supply of oxidizer to the reaction zone and the loss of heat from the reaction zone. These competing mechanisms play a very important role in the end region of the sample where buoyancy generated currents can enhance the smolder reaction or produce its extinction, depending on whether the incoming reaction is strong and oxygen limited, or weak and sensitive to heat losses. A paper reporting this work has been presented at the 1990 Fall Technical Meeting, WSS/CI.

A concurrent effort to study smoldering in the presence of a gas/solid interface, and the phenomenon of the transition to flaming has recently been initiated. The experiments are conducted in a small scale combustion tunnel that has been already built and is fully operational.

2) Microgravity Experiments

A series of opposed flow smoldering experiments have been conducted in the KC-135 aircraft (30 secs of micro-g for up to 40 parabolas) to observe the effects of the variation of the gravity on the smolder process. Although the micro-gravity period is too short to study smoldering in micro-gravity, the tests have provided initial information about the process and permitted the observation of smolder trends as the gravity changes. The tests also complement the Drop Tower tests previously conducted at the NASA LeRC 2.2 seconds tower. The results show that buoyancy affects both the species transport and transfer of heat to and from the reaction zone. At the reaction zone the former is dominant, which results in a decrease of the smolder temperature in microgravity. Away from the reaction zone the latter is dominant and the temperature increases due to the lack of convective cooling. All these effects are less noticeable as the flow velocity is increased, and as the reaction propagates toward the sample interior confirming that buoyancy is important at low flow velocities and near the sample ends. A paper reporting this work has been presented at the 1990 Fall Technical Meeting, WSS/CI.

Finally, the information obtained from these experiments on the smoldering of polyurethane foam has been used to design a small scale experiment to be carried out in the USML-1 mission scheduled for March 1990. The size of the fuel specimen (a cylinder 5cm in diameter and 10 cm long) is determined by the size of the Glove Box where the experiments will be conducted. Four tests are planned, two in still air and another two with a low velocity flow. Two igniter configurations will be used, one with the igniter at the cylinder axis and the other with the igniter at one end of the cylinder.

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Time-Dependent Computational Studies of Premixed Flames in Microgravity

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October 1989- October 1990

Objectives: The objective of this research is to investigate fundamental problems in the combustion of premixed gases such as the differences in the propagation and extinction of gas-phase flames in zero and normal gravity.

Research Task Description: We study the dynamics of premixed flames by performing detailed numerical simulations using a time-dependent, two-dimensional numerical model. This model solves the multispecies coupled partial differential reactive flow equations. The model includes detailed chemical kinetics mechanisms, algorithms for thermal conduction, molecular diffusion, viscosity, heat conduction to walls, convective transport and effects of gravity. We also evaluate various simplified models by comparing their predictions to those from detailed simulations.

Progress to Date: Calculations of the cellular structure of lean hydrogen flames show that cell-splitting, as observed in experiments, is predicted for sufficiently reactive mixtures. The structures that evolved also resembled the cellular structures observed in experiments. The simulations further indicated that the "cell-split limit" postulated from experimental observations is an intrinsic property of the mixture and that external losses are not necessary to cause this limit. However, for quantitative predictions of the cell-split limit we may need to account for losses and three-dimensional effects. In another series of simulations, the effects of gravity on the stability and structure of flames in a 51 mm channel was studied. These simulations show that the effects of gravity become greater as the lean flammability limit (for hydrogen) is approached and that cellular structures that are present in zero-gravity can be suppressed by the effect of buoyancy for very lean hydrogen-air mixtures. Furthermore, these simulations have provided additional insight on the interactions between the processes leading to cellular structure and the buoyancy-induced Rayleigh-Taylor instability mechanism. Currently we are studying the effects of heat losses and viscosity on the structure and dynamics of multidimensional flames.

Publications

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Patnaik, G. and Kailasanath, K., "Effect of Gravity on the Stability and Structure of Lean Hydrogen-Air Flames", in *Proceedings of the 23rd (International) Symposium on Combustion*, The Combustion Institute, Pittsburgh, PA., 1990.

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Radiative Ignition in Microgravity Environment

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Dr. Howard R. Baum

Objectives: The objective of this study is to develop a theoretical model capable of predicting the radiative ignition of a cellulosic material (for example, filter-paper) and the subsequent flame spread over the sample in a microgravity environment. This study is to lead to applications such as fire safety for spacecraft by understanding and predicting ignition and subsequent flame spreading behavior. It is hoped that validation experiments of the predicted results will be conducted in a microgravity environment in the next phase of the study.

Research Task Description: This study consists of four parts: (1) Thermal and thermal oxidative characterization of the cellulosic material will be measured in a normal gravity environment by using a thermal analysis technique. A global degradation scheme involving two or three step reactions will be used and their kinetic constants will be determined by dynamic derivative thermogravimetry at various heating rates and also at various ambient oxygen concentrations. (2) Kinetic constants of global gas phase oxidation reactions of evolved degradation products from the degrading cellulosic material will be determined in a normal gravity environment by using a well-defined laminar high temperature flow reactor or calculated assuming OH equilibrium. (3) A theoretical model of ignition of the cellulosic material by an external radiation and subsequent transition to flame spreading in a microgravity environment will be developed and solved numerically using the above characteristics of the degradation and of the global gas phase oxidation reactions. The advantage of a microgravity environment is fully utilized (the dominant vorticity creation mechanism in the bulk of the gas is absent), permitting the gas phase flow pattern to be calculated by solving an irrotational flow pattern determined by the thermal expansion of the field and the convective mass transfer of the evolved degradation products to the gas phase. (4) Radiative ignition experiments at a normal gravity environment will be conducted to examine ignition behavior and also to obtain radiative properties of the cellulosic material. The bottom surface of the sample will be ignited by a vertically upward external radiation. Ignition behavior in this configuration in a normal gravity environment is the closest to that in a microgravity environment.

Progress to Date: The degradation kinetics of the paper has been determined by conducting derivative thermogravimetric analysis with evolved gas analysis of CO, CO₂, H₂O, and O₂ and sample weight loss rate at 4 different heating rates and 4 different gas phase oxygen concentration. The kinetic constants of three global degradation reactions were determined; first for pyrolysis reaction of the cellulosic material, second for oxidative degradation of the cellulosic material, and third for oxidative degradation of char. The first and the second reactions form char and evolved gases. The values of activation energy, pre-exponential parameter, and order of reaction were determined for each reaction. The product yields for each reaction are being determined. The first reaction is endothermic and the second and the third reactions are exothermic. The value of the exothermic reaction and the values of the exothermic reactions were determined by DSC.

A numerical code to calculate ignition and subsequent flame spread in a quiescent environment have been developed by adding a one-step gas phase oxidation reaction to our previous pre-ignition model with thermal degradation of the cellulosic material. This model consists of coupled velocities, temperature, and species equations in the gas phase and the three coupled global degradation reactions in the cellulosic material. The results show that a brief ignition can occur in air at external radiant flux of 5 W/cm² but it does not sustain a flame spread. In a 35% oxygen atmosphere, however, the transition from ignition to

flame spread occurs and flame continues to spread over the sample surface. Initially, the shape of the flame is umbrella-like at the center. However, the center portion of the flame gradually disappears; probably due to lack of fuel supply from the charred sample surface. The flame becomes gradually smaller taking the shape of a small ring spreading radially outward. After the disappearance of the center portion of the flame, oxygen gradually diffuses back to the hot char surface and glowing of the char is observed at the center portion of the char surface. The limited number of runs performed to date indicates that ignition and transition to flame spread is sensitive to oxygen concentration in the atmosphere, but not to the supply of fuel gases in the conditions studied.

Publication

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Effect of Low Velocity Forced Flow on Flame Spread Over a Thermally-Thin Fuel in the Absence of Buoyancy Induced Flows

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In-House

Objectives: The objective of this program is to determine the extinction limits and steady burning characteristics of thermally-thin solid fuels over a wide range of oxidizer concentrations and flow velocities. This work will provide insight into the effects of buoyancy on flame spread mechanisms by decoupling natural convective transport processes from forced convective, conductive, and diffusive transport processes that are important in spreading flames. Understanding the mechanisms for flame spread will provide a fundamental link between normal gravity materials flammability and materials flammability in spacecraft environments where low velocity forced flows exist due to environmental control systems.

The approach used in this study is to perform a series of experiments in low gravity varying fuel thickness, oxidizer concentration, diluent composition, pressure, and opposed flow velocity. Tests are conducted in a low speed combustion tunnel developed for use in all three NASA Lewis Research Center's low gravity facilities. Low gravity is required for these experiments because in normal gravity buoyancy-induced gas flows around the spreading flame are on the order of or greater than the range of forced flow velocities to be studied (0-30 cm/s). These natural convective flows overwhelm or combine with the forced convective flows so that the effect of the forced flow on the flame spread rate cannot be isolated.

Progress to Date: Results to date include quiescent flame spread and extinction results which defined an extinction boundary where quenching and blowoff extinction boundaries meet at a low oxygen limit for flame spread in opposed flow. Forced flow flame spread experiments at three different oxygen concentrations have shown that flame spread rate increases dramatically with opposed flow from the quenching (low velocity) extinction limit to a peak flame spread rate at intermediate opposed flow velocities of 15-20 cm/s. For higher opposed flow velocities, the flame spread decreases until blowoff (high-velocity) extinction occurs. At high enough ambient oxygen concentrations (30% by volume for fuel studied) a wide plateau is observed in the flame spread rate - opposed flow curve where the flame spread rate is independent of opposed flow over a wide range of intermediate flow velocities.

Based upon these results, a flame spread map has been derived as a function of ambient oxygen concentration and opposed flow velocity which indicates three distinct regions where different mechanisms control the flame spread process. In the near-quenching region (at very low opposed-flow velocities and/or low oxygen concentrations), a new controlling mechanisms of flame spread - oxidizer transport-limited chemical reaction - is proposed. In the near-blowoff region, high opposed flow velocities impose residence time limitations on the flame spread process. A critical characteristic relative velocity line between the two near-limit regions defines conditions which result in maximum flammability both in terms of peak flame spread rate and minimum oxygen concentration for stable burning. In the third region, away from the extinction boundary, flame spread is controlled by gas-phase conduction, and is adequately described by thermal theories of flame spread.

The new mechanism of oxygen transport-limited flame spread has been proposed for the near-limit low velocity Flame spread region, which is unique to low gravity environments. It is suggested that the transport-limited heat generation rates, when compared to the significant heat loss rates, control the flame spread process in this region, and heat generation/heat loss ratio reaches a critical value at the quenching extinction limit.

Microgravity quiescent flame spread experiments in various oxidizer-diluent atmospheres indicate that the primary effect of the diluent gas in the near-quenching region is to modify the heat losses from the flame. This changes the critical ratio of heat generation to heat loss and thus shifts the extinction limit. The use of carbon dioxide as diluent (which has strong gas-phase radiative characteristics and a higher heat capacity, both of which are net heat losses for these weak flames) causes flame extinguishment at much higher oxygen concentrations than nitrogen. Helium, due to its high thermal diffusivity, has high conductive heat losses and despite its lower heat capacity, also extinguishes flames at higher oxygen concentrations than nitrogen. Argon, which has the same thermal diffusivity as nitrogen, causes the flames to extinguish at lower oxygen concentrations because of its lower heat capacity and lower thermal conductivity, both of which reduce heat losses from the flame.

Forced convective flame spread results and quiescent oxidizer-diluent mixture extinction results were presented at a poster session of the Twenty-Third Symposium (International) on Combustion in July, 1990. The forced convective flame spread results have been accepted for publication in *Combustion Science and Technology*. Preparation of a manuscript of the diluent extinction results is underway. A new proposal for a flight experiment on "Low-Velocity, Opposed-Flow Flame Spread in a Transport-Controlled, Microgravity Environment" was submitted to OSSA against the Combustion NRA in March of 1990 by Altenkirch, Olson, and Bhattacharjee.

Further analysis and ground-based experiments will be conducted in opposed flow flame spread to better define the critical ratio between transport-limited heat generation to heat losses. If the NRA proposal is funded, a Science Requirements Document for space-based experiments will be prepared.

Publications

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Mechanisms of Combustion Limits in Premixed Gas Flames at Microgravity

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NAG3-965 (NASA Contact: Dr. Karen Weiland, LeRC)

Objective: The objective of this work is to gain understanding of the mechanisms responsible for limit phenomena in premixed gas combustion processes. By employing microgravity experiments it is possible to eliminate the complicating and sometimes ambiguous influences of buoyant convection on these phenomena.

Research Task Description: Three types of limit phenomena have been identified which may be affected by buoyant convection: flammability limits, ignition limits, and stability limits. The effects of the interactions of chemical reaction, thermal and mass diffusion, flame front curvature, and radiative transport are being examined. Additionally, newly discovered μg limit phenomena, not observable at earth gravity, are being investigated.

Progress to Date: We have found in previous work that lean H_2 -air mixtures exhibit unusual flame propagation modes at μg including cellular structures and in some cases stable, stationary, non-propagating spherical flames ("flame balls"). Our theoretical studies have shown that these result from the interactions of flame front curvature, gas radiation, and Lewis number (Le) effects. In recent experimental work, it has been found that the same behavior is found in lean H_2 - O_2 - CO_2 mixtures and H_2 - O_2 - SF_6 and CH_4 - O_2 - SF_6 mixtures of any stoichiometry. These results indicate that the Le of the mixture is the overriding factor in the mechanisms of these phenomena. Previous studies have been conducted in a drop tower providing only 2.2 seconds of μg , which is insufficient for most studies of "flame balls." Recent μg experiments performed on NASA's KC-135 aircraft have shown that these structures appear to be stable for long periods of time (≈ 15 sec). With infrared imaging, we have observed these structures without the "coloring" agents needed previously; this simplifies quantitative comparison with numerical calculations. The "g-jitter" in the aircraft experiments caused a new phenomena to appear: "Flame cylinders" resulting from moving "flame balls" which later break into "flame balls." While theory shows that steady "flame cylinders" are not possible, it also suggests that such structures can persist for relatively long periods of time. Future efforts include further experimental and theoretical investigation of "flame cylinders," and the influence of inert, radiating particles which may affect the optical thickness of the mixture.

A new phenomena described in last year's progress report, namely that of "double flames" in rich H_2 - O_2 - CO_2 mixtures, have been investigated further. In "double flames," after ignition a relatively fast spherical flame front traverses the entire chamber and disappears upon reaching the vessel walls. It is then immediately followed by another flame with a slightly high velocity and generating a higher temperature than the first one. Recent experiments, in which gas samples were extracted from the products during the free fall, indicate that the first flame consumes only two-thirds of the oxygen and produces equilibrium CO (due to the water-gas shift), then the second flame consumes most of the remaining O_2 . Pressure and temperature records are consistent with the gas sampling results in terms of the observed heat release. Apparently some O_2 "leaks" through the flame front (although the mixture is rich in H_2 overall) and later reignites with the excess H_2 when the temperature and pressure of the burned gases has risen enough, producing a second flame front.

Yet another unusual phenomena has been observed in rich C_3H_8 - O_2 - CO_2 mixtures: the simultaneous appearance of small sooting cells, medium sized slowly propagating "Flame balls" and fast

elongated flamelets. Even more surprisingly, as these mixtures were diluted, a flammability limit was reached (as expected), but if the mixture was diluted still further, it became flammable again! Further dilution caused permanent non-flammability. No explanation has been found for this behavior, which we have termed "dilution-enhanced flammability."

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Presentation

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Ignition Delay and Flame Spread Above a Liquid Fuel Pool.

University of California
Professor W. A. Sirignano
Mr. D. N. Schillel
Dr. F. H. Tsau

Objectives: This study is intended to investigate the relative importance of buoyancy and surface tension on ignition delay and flame spread above an axisymmetric liquid fuel pool. By studying the heat and mass transport mechanisms which control ignition delay and flame spread rates, we hope to gain knowledge which may be used to prevent liquid fuel pool fires. When a liquid fuel is initially below its flash point temperature, heat and mass transport in the liquid phase (governed by a combination of buoyancy and thermocapillary forces) is important because the liquid fuel must be heated sufficiently to create a combustible mixture of fuel vapor before ignition and flame spread can occur. The coupling of buoyancy and surface tension in the gas phase is also important in the transport of fuel vapor to the ignition source, and the subsequent heat and mass transport during the flame spread process. On account of nonuniform heating from above due to the ignition source or the flame, liquid motion will be driven by both surface-tension gradients and by buoyancy. If only liquid motion were considered, then since these driving forces generally support in concert surface fluid motion away from the heat source, one would be led to believe that increasing either buoyancy or surface tension would delay ignition yet support flame spread (as the convection assists the preheating process ahead of the flame). However, in the gas phase, buoyancy-driven convection opposes the surface-tension-driven motion. Buoyant convection opposes conduction of heat to the liquid surface yet assists transport of fuel vapor toward the heat source. In contrast, thermocapillary-driven circulation above the liquid surface assists conduction of heat to the liquid surface but opposes diffusion of fuel vapor toward the heat source. The result is that liquid surface temperatures are greater at reduced gravity, but the fuel vapor is swept radially outward near the liquid surface by the thermocapillary-driven circulation in the gas phase. Therefore, increasing gravity could lead to shorter ignition delay since fuel vapor is transported quickly to the ignition source by buoyancy forces.

In addition to the axisymmetric problem, we are studying associated three-dimensional phenomena including the effects of g-jitter and liquid surface curvature. These are especially relevant in low-gravity environments in which future experiments might be performed.

Research Task Description: Numerical modelling is used to investigate the aforementioned problems. At the NASA Lewis Research Center, experiments are performed in both normal gravity and reduced gravity environments in order to validate the numerical models and to add insight into the problems. The fundamental aspects of the axisymmetric study have been investigated in various enclosed and open pool configurations. Parameters which have been varied include gravity level, surface-tension coefficient, radiation, geometry and temperature of the ignition source, height of the liquid, and properties of the liquid.

Progress to Date: During the past year, five papers were written on the axisymmetric problem without the effects of chemical kinetics (i.e., studies of the heat and mass transport in the preignition processes). The first paper was published and presented at the 26th ASME/AICHE Heat Transfer Conference (Schiller, Sirignano, and Abramzon, 1989). In this paper, two-phase simulations were made at normal gravity to investigate the effects of variable properties and vaporization on the enclosure problem. Some of these results were then incorporated into a two-part paper which was recently accepted by the Journal of Thermophysics and Heat Transfer (Schiller and Sirignano, 1991). In Part I of this paper, the coupling of buoyancy and thermocapillarity was studied in the liquid phase. In Part II, the transport of heat and mass in

the gas phase was suggested to be an important factor in ignition delay. A fourth paper featuring a comparison of the numerical and experimental studies at normal and reduced gravity levels (primarily for a gas-only enclosed configuration) was submitted to the Journal of Thermophysics and Heat Transfer in September 1990 (Ross et al., 1991). Finally, results of an open pool geometry were presented at the 29th AIAA Aerospace Sciences Meeting (Schiller and Sirignano, Reno, Nevada, January 7-11, 1991). A 3-D code has been used to examine the effects of g-jitter for a range of jittering frequencies and different gravity levels. The effect of each individual gravity component on the overall heat transfer is also studied. Results of the 3-D code was presented earlier this year at the 28th AIAA Aerospace Sciences Meeting (Tsau, Elghobashi, and Sirignano, 1990). An updated version of this paper was submitted July 1990 to the Journal of Thermophysics and Heat Transfer (Tsau, Elghobashi, and Sirignano, 1991).

Future work on the axisymmetric problem will concentrate on incorporating chemical kinetics into the numerical model. Since the chemical reaction time is much smaller than the maximum convective time step, a split-operator scheme for incorporating chemical reactions will be investigated. In this method (which is also called the method of fractional steps), two operators are used to handle the fluid-mechanical and the chemical contributions to the rate of change of species (solved in terms of mass fraction Y_i). For these variables, the governing equations may be written in the form

$$\frac{\partial \phi}{\partial t} = L_{tr}(\phi) + L_{ch}(\phi)$$

where $L_{tr}(\phi)$ is the transport operator, which is solved over one transport time step (solution of the species equations without the source terms due to chemical kinetics), and $L_{ch}(\phi)$ is the chemical operator, which yields first order differential equations that are solved over many smaller chemical time steps. The order of the operators is reversed after each step, so that after two transport steps, the solution can be written as $\phi^{k+2} = L_{tr}L_{ch}L_{ch}L_{tr} \phi^k$.

Publications

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Tsau, F. H., Elghobashi, S. E., and Sirignano, W. A., "Effects of G-Jitter on a Thermal, Buoyant Flow," Paper No. 90-0717, *28th AIAA Aerospace Sciences Meeting*, Reno, Nevada, Jan. 1990.

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Combustion of Solid Fuel in Very Low Speed Oxygen Streams

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Professor James S. T'ien
Kurt R. Sacksteder (NASA Lewis RC)
NAG 3-1046

Objectives: The objective of this research is to study the fundamental characteristics of flame spreading and extinction processes of solid fuels in very low speed concurrent flow.

Research Task Description: The task includes performing both experiments and theoretical modeling work for concurrent-flow flame spread over solid fuel. The flow will be in the low speed regime unobtainable in normal gravity buoyant condition. Both low speed forced flow and buoyant flow in reduced gravity will be included.

Progress to Date: Experimentally, we have conducted a series of tests in low-speed forced flows from 0-5 cm/sec using thin tissue papers. This is conducted using a sample translation device and the 5-seconds drop tower. The variables changed in these tests are the ambient oxygen percentage and the forced flow speed. It is observed that the visible flame lengths are much smaller at low concurrent flow speed than those in natural-convective flow in normal gravity. The flame length increases with flow speed and oxygen percentage. Flame becomes extinct when oxygen percentage or flow velocity becomes too low. The flame extinguishes by shrinking its length with the leading edge always attached to the fuel burnout front. This is different from the extinction behavior at high speed. An approximate flammability map is constructed. However, because of the slow response of near-limit flames, more accurate boundary determination will require longer microgravity test time.

Preparation for experiments in partial gravity is being made. These tests will be conducted in airplanes flying special trajectories. The design and manufacturing of the optical system for flame measurement is underway.

For the modeling, we use the complete two-dimensional Navier-Stokes equations for the gaseous flame in order to be able to treat both forced and buoyancy flows and to study both flame spread and extinction characteristics. The gas phase equations are coupled to the thin solid fuel through a solid energy balance equation and pyrolysis law. The system of equations has been formulated, the computer program has been written. We are near the completion of checking the various elements in the algorithm.

Publications

T'ien, J.S., "The Possibility of a Reversal of Material Flammability Ranking from Normal Gravity to Microgravity," Comb. & Flame 80, 335-357 (1990).

Ross, H.D., Sotos, R.G., and T'ien, J.S., "Observation of Candle Flames under Various Atmospheres in Microgravity," Comb. Sci. Tech., in press.

Sacksteder, K.R., "The Implications of Experimentally Controlled Gravitational Accelerations for Combustion Science," *Twenty-Third International Symposium*, 1990, in press.

Presentations

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Sacksteder, K.R., "Spacecraft Fire Safety - The NASA Perspective," *National Fire Research Agenda, ASME Winter Annual Meeting*, San Francisco, CA, December 12, 1989.

Scientific Support for a Proposed Space Shuttle Droplet Burning Experiment

University of California, San Diego
Professor Forman A. Williams
Professor Frederick L. Dryer, Princeton University
NAG3-1081 (NASA Contact: J.B. Haggard, LeRC)
October 3, 1989 - November 30, 1991

Objectives: The general objective of this program is to ascertain how best to utilize reduced gravity facilities to pursue scientific investigations of droplet combustion. The scientific objective is to provide scientific support for development of a droplet combustion experiment module for conducting experiments in the NASA LeRC microgravity facilities, and possibly aboard a space-based platform such as the space shuttle or in the Space Station. The planned experiments are intended to improve fundamental understanding of droplet combustion phenomena, especially in relationship to time-dependent characteristics such as extinction. The scientific support objective encompasses data acquisition and reduction as well as to providing asymptotic and numerical modeling for interpretation of observations.

Research Task Description: The research tasks include theoretical modeling using asymptotics and numerical techniques, with emphasis on transient phenomena, detailed chemical kinetic and transport effects, ground based experimentation on droplet burning in both the 2.2 and 5.5 second NASA LeRC drop towers, support to NASA in providing advice on hardware aspects of a flight experiment and analysis of data to be obtained from all experiments. The modeling addresses questions related to transient burning, to soot formation and destruction, to droplet disruption, and to ignition and extinction phenomena. Ground-based experiments have been focused on droplet ignition and on impulses imparted to droplets by ignition sparks; spark designs for minimum impulse were addressed. In addition, drop tower experiments are addressing burning-rate measurements and mechanisms of soot production and of droplet disruption, as well as extinction phenomena. Work has encompassed n-decane, n-heptane, and methanol as fuels in oxidizer/inert mixtures at pressures about 0.2 and 2 atmospheres.

Progress to Date: In this work we have obtained data on the spherically symmetric burning of decane, heptane and methanol droplets in a range of ambient environments. The importance of the interaction between the spark and the droplet in the ignition of a droplet was established. Also, the importance of soot formation and how it influences the burning characteristics of hydrocarbon fuel droplets were demonstrated. Disruptive phenomena in droplet combustion were recorded and explained. The development of methods to employ a digital data processing technique for analyzing droplet combustion data was completed, and this was applied to droplet-burning data from drop towers. Identification of product dissolution in the liquid phase of a droplet was made, and clarification of histories of impurity buildup in the liquid during droplet combustion was achieved. Identification of a new 'slow' burning regime for hydrocarbon fuel droplets resulted from this joint research. In recent experiments it was found that the oxygen index limit for droplet combustion in microgravity is lower than in normal gravity.

Publications

Williams, F.A., "The Role of Microgravity Research in Contributing to the Theoretical Foundation of Combustion," in *Proceedings of VII European Symposium on Materials and Fluid Sciences in Microgravity*, ESA SP-295, 453-357 (1990).

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Shaw, B.D. and Williams, F.A., "Theory of Influence of a Low-volatility, Soluble Impurity on Spherically-Symmetric Combustion of Fuel Droplets," Int. J. Heat & Mass Transf. **33**, 301-317 (1990).

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7. EXPERIMENTAL TECHNOLOGY

Residual Acceleration Data on IML-1: Determination of Experiment Sensitivity and Efficient Data Dissemination

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Center for Microgravity and Materials Research
Dr. J. Iwan D. Alexander
NAG8-759 (NASA Contact: Dr. R. S. Snyder, MSFC)
March 1989-February 1992

Objectives: The objective of this research is to develop a mission-specific residual acceleration data reduction and dissemination plan. It will be designed to meet the needs of individual experimenters and result in a useful, manageable data base. This will enable the principal investigators to assess the acceleration environment to which their experiment was exposed, without having to examine the entire acceleration history recorded during the experiment (400 Mbyte/disk, some 20 disks/mission).

Research Task Description:

1. Identification of sensitive experiments and sensitivity ranges (magnitude and frequency) through order of magnitude estimates and the results of numerical modelling.
2. Research and development toward a plan for reduction and dissemination of residual acceleration data.
3. Use of a "Shuttle Motion Model" to predict accelerations arising from specific Shuttle maneuvers.
4. Supplementation of recorded data with calculated predictions for gravity gradient and other accelerations resulting from the basic orbital motion.
5. Implementation on existing acceleration data bases.

Progress to Date: Several specific experiments and general experiment classes have been identified as potentially sensitive to perturbations of the low-gravity environment in an orbiting laboratory:

Critical point experiment (CPF)
Crystal growth from solution (TGS/FES)
Growth of mercuric iodide from the vapor (VCGS/MICG)
Casting and solidification technology (CAST)
Protein crystal growth. (PCG)
Gravitational plant physiology experiment (GPPF)
Organic crystal growth experiments (OCGF).

Results from order of magnitude analyses and numerical simulations indicate that low frequency and steady accelerations may be of concern. Alexander (1990) gives a thorough review of our current understanding of experiment sensitivity to residual accelerations.

The research and development aspects of the data reduction plan have progressed and a prototype plan was implemented on the Spacelab 3 (SL3) accelerometer data base. Discussions of the basic analysis techniques used and the results achieved to date are included in the publications. In addition, we have attended and presented summaries of our processing techniques and results at several Microgravity Measurement Group (MGMG) and IML-1 IWG meetings.

The two-level data reduction plan developed will enable principal investigators to create a limited, user-specific accelerometer data base that can be easily merged into the post-flight experiment

analysis process. In addition, the processed data, particularly that associated with specific crew activities, will contribute to the characterization of the acceleration environment of the Orbiter. Comparison of windows of the SL3 data with data collected on other orbiter missions has already led to the identification of acceleration signatures related to specific structures and pieces of equipment in the orbiter Columbia. With the flight of IML-1, the acceleration environment characterization process can be expanded to the orbiter Atlantis.

In general, three main features of residual acceleration data can be used to characterize the acceleration environment. These features are the **time history** of the data (maximum values, mean values, acceleration vector magnitude, and particular disturbance patterns), the **frequency** components present in a given window of data, and the **orientation** of the acceleration vector during that time window. These features of residual acceleration data also play an important role in the creation of user-specific databases and in the post-flight processing of experimental results in conjunction with accelerometer data.

The amount of data processed and the form in which it will be most useful to individual PIs will depend on the particular experiment. The first level of our two-level data reduction plan identifies factors specific to an experiment that will be important in the evaluation of the needs of the investigator. The second level of the data reduction plan involves actual data processing based on the results of the first stage of the plan. The processing done at this level will result in limited, user-specific accelerometer data bases that principal investigators can use in the post-flight analysis of their experimental results. Some particularly useful data processing techniques are discussed in publications 3-5.

The current phase of our work involves the identification of specific processing techniques that will be useful for principal investigators in the post-flight analysis of experimental results in conjunction with accelerometer data. In particular, we have focused on data decimation to enable the investigation of low frequency information from long time histories and on cross-correlation analysis to identify causal relationships between accelerations and experiment perturbations.

Publications

Alexander, J.I.D., "Low-gravity Experiment Sensitivity to Residual Acceleration: A Review," Microgravity Sci. Technol. **3**, 52 (1990).

Rogers, M.J.B. and Alexander, J.I.D., "Analysis of Spacelab 3 Residual Acceleration Data," J. Spacecraft and Rockets, 1991, accepted for publication.

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Rogers, M.J.B. and Alexander, J.I.D., "Cross-correlation Analysis of On-orbit Residual Accelerations in Spacelab," AIAA Paper 91-0348, presented at the AIAA 29th Aerospace Sciences Meeting, 7-10 January 1991, Reno, Nevada.

Acoustic Containerless Science

Jet Propulsion Laboratory
Dr. Martin Barmatz
NAS7-918
October 1, 1981 - September 30, 1991

Objectives: The objectives of this task is to apply previously developed acoustic levitation concepts to study the containerless processing of glasses and ceramics using microwave heating techniques. The task objectives will include (1) determination of reaction mechanism, microstructure development and physical properties associated with containerless microwave synthesis of glasses and ceramics, (2) development and application of non-contact microwave techniques for (a) monitoring the energy absorption during processing and (b) measuring thermophysical properties of containerlessly positioned samples, and (3) theoretical modeling of the acoustic and microwave field effects on materials being processed.

Research Task Description: There is a recognized need to produce advanced refractory ceramics that have higher melting temperatures and improved mechanical properties (such as strength and toughness). In recent years, ground-based experiments using microwave heating have demonstrated enhanced rates of sintering of ceramic materials leading to new microstructures. Feasibility studies on microwave heating capabilities in our laboratory have also clearly demonstrated the potential use of microwaves for controlled materials processing. The containerless synthesis of ceramics in a microgravity environment could provide the opportunity to produce contamination free ceramics with controlled microstructures. Microwave processing can heat many glass and ceramic compositions very rapidly to high temperatures, it can heat them more uniformly than other methods, and it is energy efficient. These microwave characteristics are ideally suited for microgravity studies where processing time and available power are at a minimum. By appropriate monitoring of the microwave parameters during processing one can measure various sample properties (such as the real and imaginary components of the dielectric constant) as well as obtain energy absorption information which can be used to characterize the sample reaction and densification mechanism.

Progress to Date: The previously developed theory for the shape of an acoustically positioned drop in a single mode cavity was extended to apply to the DPM triple axis positioner. Drop shape analyses were performed in preparation for a test of the theory during the USML-1 flight of the DPM module. Levitation studies at high ambient pressures were carried out up to 20 atmospheres. These studies demonstrated improved sample stability at higher ambient pressures predicted by oscillational instability theories, and agreed with the enhanced force predictions of levitation theories. Successfully demonstrated controlled microwave heating of various materials in a cold walled cavity up to 1000°C.

Publications

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Noncontact Temperature Measurement and Acoustic Levitation Development

Intersonics, Incorporated

Dr. Charles A. Rey

NAS8-37592 (NASA Contract: Buddy Guynes, MSFC)

September, 1989 to September, 1990

The task directives under this contract include but are not limited to the Division of Amplitude Polarimetric Pyrometer (DAPP), the Noncontact Temperature Measurement System Brassboard (NCTM) and the High Temperature Acoustic Levitator (HAL).

The work accomplished on the Division of Amplitude Polarimetric Pyrometer (DAPP) portion of this contract is summarized as follows:

Project Summary

The primary objective of this program was to develop an instrument to measure, instantaneously, the true surface temperature of freely radiating bodies based on measuring both the spectral emissivity and the apparent temperature (pyrometry) using polarization techniques. The design, fabrication and preliminary testing of the breadboard Division of Amplitude Polarimetric Pyrometer (DAPP) demonstrates the feasibility of this approach. The spectral emissivity is determined by performing time-resolved measurements of all four Stokes vectors of laser light reflected from the target surface. This determines the spectral emissivity and optical constants of the target surfaces in real-time. The instrument has been calibrated and tested at 0.6328 μm . The absolute accuracy of Stokes vector measurement is 0.5 - 1% at 0.6328 μm . The absolute accuracy of spectral emissivity measurements is 0.5%. The DAPP is probably the first absolute thermodynamic temperature and optical property measuring device to be made available.

Project Objectives

- a. Demonstrate the feasibility of a polarimetric method to measure precisely the spectral emissivity and optical properties of specular and partly specular surfaces. The emissivity measured by the instrument would be used to make corrections to radiometric measurements (made by a conventional pyrometer) to determine the true surface temperatures of freely radiating bodies.
- b. Design, fabricate, calibrate, and test such an instrument for materials processing and optical property measurement in containerless experiments.
- c. Deliver a prototype instrument to NASA for evaluation.

Characteristics of DAPP

A laboratory DAPP has been designed constructed and tested. This instrument has the following characteristics and specifications:

PRELIMINARY SPECIFICATIONS AND CHARACTERISTICS OF DAPP
OPERATING WAVELENGTH 633 nm

1. Polarization State Accuracy: - Radiation Detection Accuracy

Quantity	Error (Absolute Units)
S_1	0.009
S_2	0.010
S_3	0.008
Amplitude, ψ	0.05°
Phase, Δ	0.05°
Azimuth, x	0.05°
Ellipticity, α	0.05°
Axial Ratio	0.05°
Deg. of Polarization, p	0.005

2. Optical Property Accuracy: - Material Properties

Based on Measurements on Si & Mo

n	1-2%
k	1-2%
Spectral Emissivity	0.5-1%

3. Temperature Properties Accuracy:

Estimated Temperature Accuracy: ± 2 K at 1300 K.

Estimated Temperature Resolution: ± 1 K at 1300 K.

4. General Instrument Characteristics:

Response Time: 1-10 ms per emissivity measurement.

Target Distance: 12-30", variable.

Requires IBM computer interface and A/D card.

Conclusions

We present below, scientific and technical conclusions that derive from our experience in the design, fabrication and preliminary testing of a prototype DAPP device to demonstrate the feasibility of this technique for emissivity measurements of solid and liquid surfaces.

1) The DAPP can measure all four Stokes parameters of arbitrarily polarized light instantaneously, and permit fast, time-resolved polarimetry, ellipsometry and spectral emissivity measurements, ultimately leading up to fast temperature measurement.

2) The accuracy of Stokes parameter measurement is 0.5 - 1% at the laser wavelength of 0.6328 μ m. The errors are attributed to imperfections present in the retarding elements, and not the instrument design.

- 3) The accuracy can be improved with use of a better polarization state generator. Alignment at longer wavelengths would be more critical than at shorter wavelengths where the angular acceptance of the polarizing elements are greater.
- 4) The spectral emissivity can be measured to within 0.5% or better, and the indices of refraction are accurate to within 1%. These are worst case estimates and the values are based on measurements on silicon at room temperature.
- 5) The high accuracy in spectral emissivity measurements will enable the true surface temperature to be determined to within 0.5% when the instrument is used concurrently with a radiometric measurement such as a standard commercial pyrometer.
- 6) Safe, non-visual and accurate alignment of the instrument was achieved with the use of two quadrant detectors. This provided a very high degree of reproducibility in alignment and positioning of the instrument for laboratory use.
- 7) The DAPP has been calibrated by two independent methods, both of which produced nearly identical results. The 4-point method uses the bare minimum of optimized polarization states on the Poincare sphere. It is slightly less accurate compared to the equator-pole method.
- 8) Short and long-term drift tests suggest that the resolution of the instrument is better than 0.2% in any Stokes parameter. This is partly attributed to incorporation of light-modulation techniques into the design of DAPP.
- 9) The response time of the instrument, in determining the Stokes parameters is limited only by the electronics and the time required for matrix inversion and numerical reduction. Initial tests suggest that the intensity measurements could be made in a time as small as 0.1 us.
- 10) The simplicity of the design and electronics, and the ease of data reduction make it an ideal instrument for use in laboratories and in process control applications for the measurement of temperature.

The work accomplished on the Noncontact Temperature Measurement System Brassboard is summarized as follows:

The NCTM System Brassboard was completed under NASA contract NAS8-37592. The goal was to provide an infrared imaging system for noncontact temperature measurement of levitated specimens in the DPM Dual Zone Chamber experiment. The completed hardware provides a digitized version of the analog video output of an AGEMA 870 camera. This digital data is intended for downlink via the space shuttle telemetry system. For ground-based testing, additional hardware was developed to decode and convert the digital data back to analog format, thereby allowing the use of the AGEMA support electronics, computer, TV monitor, and other supporting hardware. This system provides the capability of directly acquiring digital data for precise temperature measurement of any single, selectable pixel. It is possible with this NCTM device to achieve a temperature resolution of 0.35°C under ideal conditions.

The work accomplished on the High Temperature Acoustic Levitator (HAL) is summarized as follows:

The High Temperature Acoustic Levitator (HAL) is a containerless processing module which uses a 3-axis acoustic positioning system in order to contain nonconducting as well as conducting liquid and solid materials. HAL is based on a design which has been developed through the breadboard stage and tested on the KC-135 in order to establish operating capabilities and characteristics. This acoustic positioning system

has the capabilities for providing very accurate specimen positioning and in addition producing a quiescent, spin-free and stable specimen state. The design can be readily adapted to a processing module which could be carried aboard NASA space flight facilities such as Spacelab or the Space Station.

HAL would use xenon arc or laser beam heating for high temperature containerless testing and processing studies of glass, ceramic, metal, and alloy samples in microgravity. This module would have a temperature range up to 2000°C with a design goal of at least 2700°C. It has capabilities of processing, heating, melting, soaking, cooling, and solidifying samples without the physical contact of a container. Advantages of this system include extremely stable sample positioning utilizing optical feedback, and very fast heating and cooling rates of at least 200°C/sec. Samples may be processed in a very high purity, particle free, inert, oxidizing or reducing gaseous environment. The device could accept nominally spherical samples, 2-6 mm in diameter and could perform a large number of experiments sequentially.

The sound pressure level is electronically monitored and controlled by a computer. This can be used to modulate the shape of a liquid sample in order to study fluid dynamics of drops or to measure physical properties, such as surface tension and viscosity. By properly phasing the acoustic signals between transducers, controlled spin of the specimen can be attained.

During all stages of processing, there can be continuous video and thermal imaging of the specimen from orthogonal directions. Thermal imaging can be provided at one or more wavelengths to provide noncontact temperature measurement. The open architecture of the levitator allows convenient access for diagnostic equipment.

Publications

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Containerless High Temperature Property Measurements

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Dr. Charles A. Rey

NAS8-37472 (NASA Contact: M. Robinson, MSFC)

September 1989 - September 1990

Introduction and Summary: The combination of laser polarimetry and controlled atmosphere containerless processing has allowed the generation of unique property data on undercooled liquids.

This report summarizes recent results on the titanium-aluminum alloy system. The optical properties of liquid titanium and aluminum were measured previously under this program.

Work on the alloy system was initiated for two reasons:

1. To establish the relationship between optical properties and composition for a binary alloy in which both components had been studied.

2. In collaboration with Vanderbilt University, to generate the data for undercooled Ti-Al alloys necessary to interpret the results of undercooling studies on carried out at Vanderbilt.

Experimental: Binary alloys with nominal compositions shown in Table I were prepared and analyzed by Collin Anderson and William Hofmeister at Vanderbilt University. The undercooling behavior of alloys IV, V and VI have been studied extensively by Anderson in his PhD thesis research at Vanderbilt.

TABLE I

Alloy Compositions Investigated

ALLOY	Al (atom%)	Ti (atom%)
I	95	5
II	90	10
III	80	20
IV	60	40
V	50	50
VI	40	60

Small specimens (ca. 0.3 g) were levitated and heated in an electromagnetic levitator. The specimen temperature was controlled by adjusting the ratio of He:Ar in the gas surrounding the specimen. For alloys rich in titanium, laser beam-heating was used to achieve the highest temperatures. All of the alloys were melted and heated to a temperature sufficient to clean them in the conditions which prevailed during the experiments.

The apparent temperature of the levitated specimen was monitored with two pyrometers. One instrument provided apparent temperature data and was equipped with a broadband detector capable of detecting the recalescence event. The other instrument provided apparent temperature data only.

The index of refraction, n , the extinction coefficient, k and the emissivity, e were acquired at the HeNe laser wavelength (0.633 μm) over a range of temperature. The lower experimental temperature limit

was determined by the need to maintain clean surfaces for the measurements and the upper temperature limit was determined by the temperature at which condensed vapor interfered with the ability to measure temperature.

The melting point was determined by observing the specimen during the heat-up cycle. All alloys were cooled to below their melting point with the intention of producing supercooled melts.

Results: This section presents preliminary results.

Melting Point: The following melting points were determined by observing the specimen during the optical property measurement experiments: 1613, 1675, 1717, 1775, 1795 and 1911K respectively for alloys I through VI. The melting points will be determined in separate, in-progress experiments at Vanderbilt.

Undercooling Alloys I, II and III exhibited mild undercoolings of the order of 20-30K. Alloys IV, V and VI could readily be undercooled by about 20% of their absolute melting point. Recalescence flashes were observed when these alloys solidified.

Optical Properties: Data was acquired for the undercooled liquid and subsequently on the solid at the same temperature.

Comments

The published phase diagram for the Ti-Al system shows that the melting point of aluminum is elevated rapidly when titanium is added to it. The addition of 20 atom% titanium elevates the melting point of the alloy by almost 800°. Addition of 40 atom% titanium increases the emissivity of the alloy to about the same value as pure that of pure titanium. A small titanium addition results in a decrease in emissivity, this may be due to the formation of easily accessible electron energy levels by a doping mechanism. Continued addition of titanium increases the emissivity until the near steady-state value is reached.

The emissivity of the liquid alloy was consistently found to be lower than that of the solid for alloys IV and V. The correlation between phase stability, melting point and optical properties will be explored further. The optical properties may prove to be a valuable tool in the analysis of phase behavior. The absence of supercooling alloys I, II and III suggests that the TiAl₃ phase is important in the nucleation behavior in the liquid alloys.

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Dr. A.V. Anilkumar

Objectives: The primary objective of this task is to develop a detailed and quantitative understanding of the interactions between a sample and the acoustic field in a levitation chamber in order to pursue high temperature containerless processing using advanced acoustic methods. This objective is being addressed as follows: (1) develop advanced chamber systems to provide improved chamber/waveguide coupling and impedance matching and improved sample stability and rotation control; (2) study the sample interaction with the higher harmonics generated in the acoustic field; (3) study the shaping of liquid drops by acoustic forces; (4) study the acoustic torque on a levitated sample of varying shape and position; and (5) study the effects of feedback systems on levitated sample stability.

Research Task Description: Many of the materials research experiments to be conducted in the microgravity science and applications program require manipulation and control of weightless, molten materials in a non-contaminating environment. In these experiments, the melt is positioned and formed within a container without physically contacting the container's walls. Acoustic levitation provides a versatile and powerful technique for containerless processing, but the methods developed to date are limited to moderate processing temperatures. As the sample and/or chamber temperature rises, it becomes increasingly more difficult to introduce the acoustic energy to the chamber because of a growing acoustic impedance mismatch between the chamber and sound sources (acoustic drivers). A method for improving the coupling between the sound sources (acoustic drivers) and resonance chamber of an acoustic levitation system has been developed and tested experimentally. By appropriate configuration of the system, a matched driver pair can produce a fourfold increase in the acoustic energy transferred to the chamber as compared to that produced by a single driver. This coupling improvement can be extended even further by adding more driver pairs. The actual improvement of one driver pair as compared to a single driver was determined by measuring sound pressure levels and acoustic radiation forces on rigid spheres in a rectangular resonance chamber. By using two drivers to excite the same mode in an acoustic chamber, a coupling improvement between the drivers and chamber has been demonstrated. Preliminary results also indicate that the use of opposing drivers causes the second harmonic to be suppressed. More detailed studies are in progress in order to better understand the coupling phenomenon. More complete radiation force measurements are currently underway that will provide more details of how the force as a function of input power behaves for different driver configurations. Also, the force as a function of position will be measured and compared to King's theory. The effects of second harmonic suppression on the driver-chamber coupling will also be studied. A systematic investigation of how the acoustic impedances throughout the driver-chamber system are affected by driver configuration will be initiated. Finally, more than two drivers will be used to excite the same modes to see if further enhancement is possible.

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B. FLIGHT EXPERIMENTS

1. ELECTRONIC MATERIALS

A Comparative Study of the Influence of Convection on GaAs

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Dr. David Matthiesen
Mr. Alfred Bellows
Mr. Glenn Duchene
NAS3-24644 (NASA Contact: Dr. R. Lauver, LeRC)

The objective of this study is to determine the effects of buoyancy driven fluid flow on the properties of melt grown GaAs crystals. This program is sponsored by NASA, GTE Laboratories and the United States Air Force.

A highly efficient gradient freeze growth system has been developed to grow a one inch diameter by 3.5 inch long selenium doped gallium arsenide crystal (Se/GaAs). Growth systems, with and without interface demarcation by current pulsing (IDCP) have been designed, fabricated and tested. These two growth systems have been incorporated into a fully self-contained payload which will be launched as part of the Get Away Special program. The ground based tasks of growth in the bottom-seeded vertical Bridgman, with and without IDCP, as well as the horizontal Bridgman growth, with and without IDCP, have been completed.

The payload is currently scheduled to be launched as part of the GAS Bridge on STS-40 (Columbia) in May, 1991.

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Compound Semiconductor Growth in Space

NASA Langley Research Center
Dr. A. L. Fripp
Mr. W. J. Debnam
Dr. I. O. Clark
Dr. R. K. Crouch, NASA Headquarters
In-House

Objectives: The objectives of this research are to determine the effects of gravity driven convection on the growth parameters and crystal properties of compound semiconductors.

Research Task Description: The Microgravity Science effort at the Langley Research Center is centered on the growth of the compound semiconductor alloy, lead tin telluride. Lead tin telluride is a substitutional alloy of lead telluride and tin telluride that is miscible over the entire compositional range. The semiconductor properties of this material are dependent on the ratio of the two components and consequently, the uniformity of an array of devices is dependent on good compositional control.

This material was chosen for microgravity research for a number of reasons. Lead tin telluride is not only a useful semiconductor material which has been used for construction of infrared detectors and tunable diode lasers but it also has a similar phase diagram to other compound semiconductors of interest such as mercury cadmium telluride and mercury zinc telluride. Lead tin telluride is very interesting from a purely scientific point of view in that it is both solutally and thermally unstable, but in a one dimensional analysis with growth axis parallel to the gravity vector, only one instability works, per orientation, at a time. This double convective instability cannot be made stable by balancing thermal and solutal expansion in a high temperature gradient. Lead tin telluride is amenable to study for it is easily compounded; it has a relatively low vapor pressure; it is single phase and there is existing, though limited, literature on its growth and properties.

The desired growth mode is of course one in which convection is zero so compositional steady state can be reached. However fluid dynamic calculations have shown that finite convection exists in the physical configuration used in crystal growth experiments even at 1×10^{-8} Earth gravity if there is a density gradient orthogonal to the gravity vector. However, due to the residual atmosphere the minimum gravity level expected on the Space Shuttle is roughly the order of 1×10^{-7} Earth gravity. Hence experiments are designed such that interface movement ie, growth rate, is greater than the anticipated fluid velocity.

Other work at Langley ranges from fundamental studies involving the direct measurement of both steady and oscillatory fluid flow in a crystal growth melt to efforts in furnace design and calibration. Also of interest is an effort to measure the melt-solid interface shape and position as this is of great importance to understanding the crystal growth process.

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Solution Crystal Growth in Low-g

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NAS8-36634 (NASA Contact: Mr. Rudolph Ruff, MSFC)
September 25, 1986 - December 31, 1992

Objectives: The objectives of this research project are: 1) to grow crystals of triglycine sulfate (TGS) using modified Fluid Experiment System (FES); 2) to perform holographic interferometry tomography of the fluid field in three dimensions; 3) to study the fluid motion due to g-jitter by multiple exposure holography of tracer particles, and 4) to study the influence of g-jitter on the crystal quality.

Research Task Description: This project involves a reflight of an experiment, "Solution Growth of Crystals in Zero-g," flown earlier on Spacelab-3 mission. Two experiment runs are now planned for the First International Microgravity Laboratory (IML-1) to be flown in November, 1991. The first experiment run is primarily aimed towards the study of the fluid motion using multiple exposure holography of tracer particles. This run is expected to last about 20 hr. The second run which will be about 40 hr will be used to grow a TGS crystal using a predetermined polynomial for the temperature programming of the seed crystal. The orientation of seed crystals for these runs will be either (001) or (010). Experiments have been completed to determine the proper shape and size of the seed crystals for the flight.

Experiments are conducted in the Ground Control Experiments Laboratory (GCEL) where a test cell similar to the flight is being used to grow crystals using a laboratory version of the optical system. Experiments have been conducted to determine the proper size, type, and number density of particles that should be used in the FES to monitor fluid flows. During GCEL runs, holograms are recorded with particles of 300μ , 400μ , and 600μ sizes. Different size particles are expected to diffuse at different rates enabling us to identify the particles. Proper design of holographic optical elements (HOE) has been completed. The flight windows of the FES test cells have been coated with proper HOE's. The incorporation of the HOE's will provide three independent views of the fluid field and the growing crystal. The central part of the optical windows is left uncoated for real-time monitoring using schlieren technique.

The space grown crystals will be characterized for defects by high resolution synchrotron radiation imaging and laser scattering techniques. To evaluate the device performance of the crystals, various properties, such as, dielectric constant and loss, spontaneous polarization, hysteresis loop, and pyroelectric coefficient will be measured. Infrared detectors will be fabricated and tested. All these parameters will be compared with the seed crystals and other crystals grown on ground in our laboratory and elsewhere.

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Orbital Processing of High-Quality CdZnTe Compound Semiconductors

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NAS8-38147 (NASA Contact: L. Jeter, MSFC)

August 3, 1990 - May 31, 1993

Objectives: The objectives of this research are: (1) to quantitatively evaluate the influences of gravitationally-dependent phenomena (convection and hydrostatic pressure) on the chemical homogeneity and defect density of CdZnTe crystals grown by the Seeded Bridgman-Stockbarger technique; (2) to develop high-fidelity process models of the Seeded Bridgman-Stockbarger crystal growth process, including heat transfer, fluid flow and solute redistribution, and thermo-mechanical stress; (3) to develop, conduct, and evaluate a critical flight experiment in the CGF on USML-1, including a quantitative comparison of the flight sample with 1-g simulation and ground-best samples.

Research Task Description: This experiment is to advance the understanding of Seeded Bridgman-Stockbarger crystal growth and the influences of hydrostatic, wetting, and gravitationally-dependent thermo-solutal convection on the structural and chemical quality of alloyed compound semiconductors. In the course of this program we will advance the state of seeding technology and seriously attempt to use process models for process optimization, improving the chemical homogeneity and defect densities of the material and predetermining boule orientation, increasing primary yield of high quality material for infrared applications.

Progress to Date: Three seeded CdZnTe development test experiments have been conducted in ground based facilities at Grumman and 3 seeded test experiments have been conducted on the CGF at the Ground Control Experiments Laboratory in Huntsville. Very high quality seed crystals have been machined from the crystals grown at Grumman and these have become the seeds that we will use throughout the first year of the program, and for the flight experiment. The GCEL experiments have served to empiricize the CGF thermal model and to develop seeding technology. We believe that both of these technologies are mature at this point.

Initial Seeded Bridgman-Stockbarger experiments on the Grumman programmable multizone furnace and 1-g simulation experiments on the GCEL are schedule to occur in March/April 1991. Following these tests, the flight samples will be delivered for the USML-1 flight in May 1992. The time between flight sample delivery and flight experiment will be spent developing and empiricizing the thermal, fluid-flow/solute redistribution, and thermomechanical stress models of the Seeded Bridgman-Stockbarger crystal growth process and producing an optimized CdZnTe crystal for comparison with the micro-g flight and 1-g simulation samples.

Crystal Growth of Selected II-VI Semiconducting Alloys by Directional Solidification

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The three-fold objectives of the investigation are: 1) to determine the relative contributions of gravitationally-driven fluid flows to the compositional redistribution observed during the unidirectional crystal growth of selected solid solution semiconducting alloys having large separation between the liquidus and solidus of the constitutional phase diagram, 2) to ascertain the potential role of irregular fluid flows and hydrostatic pressure effects in generation of extended crystal defects and second-phase inclusions in the crystals, and 3) to obtain a limited amount of "high-quality" materials needed for bulk crystal property characterizations and for the fabrication of various device structures needed to establish ultimate material performance limits. The effort includes both Bridgman-Stockbarger and solvent growth methods, as well as growth in a magnetic field. The work emphasizes $\text{Hg}_{1-x}\text{Zn}_x\text{Te}$ and $\text{Hg}_{1-x}\text{Zn}_x\text{Se}$ semiconducting alloys because of their potential applications for infrared detection and imaging in the 5 to 30 wavelength region. The initial experiments will use the Crystal Growth Furnace (CGF) to be flown on the first U.S. Microgravity Laboratory (USML) mission. The investigation complements the work being done on crystal growth of the $\text{Hg}_{1-x}\text{Zn}_x\text{Te}$ alloys using the Advanced Automatic Directional Solidification Furnace crystal growth system.

A number of $\text{Hg}_{1-x}\text{Zn}_{1-x}\text{Te}$ ($x=0.15$) ingots have been grown by a vertical Bridgman-Stockbarger method using existing laboratory crystal growth hardware. Precision measurements were performed to establish detailed compositional distribution maps for the crystals. Fitting these and previously obtained data to numerical solutions to a one-dimensional diffusion model was used to establish estimates for the effective liquid-liquid diffusion constants for both the HgZnTe and HgZnSe alloys. Rapid quenching experiments were performed to establish correlations between thermal conditions and melt/solid interface shapes and to obtain values for the interface segregation coefficient for the $\text{Hg}_{0.15}\text{Zn}_{0.15}\text{Te}$ alloy. Three samples of the alloy have been also processed in the Ground Control Experiment Laboratory unit of the CGF. The results from these experiments are being used to fine tune optimum temperature settings for the flight experiment. The measured compositional profiles for the samples indicated that back-melting of the samples to the desired locations, a critical requirement for the flight experiment, have been successfully accomplished.

Detailed thermal modeling of the growth process, measurements and modeling of the electrical and optical properties, and determination of some of the pertinent thermophysical and thermodynamic properties for the HgZnTe alloy system are all in progress. Preliminary growth experiments in the presence of magnetic fields have also been performed.

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The Study of Dopant Segregation Behavior during Growth of GaAs in Microgravity

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NAS8-38148

The objectives of this program are to investigate gravitational and thermal techniques for obtaining complete axial and radial dopant uniformity of the selenium dopant during crystal growth of gallium arsenide (GaAs). These techniques include controlling the thermal conditions to obtain a flat interface shape and a steady state growth rate and, most importantly, growth in the microgravity environment afforded by the Crystal Growth Furnace (CGF) in the first United States Microgravity Laboratory (USML-1).

The large hot zone length of the CGF (20 cm) should allow, for the first time in microgravity, the achievement of steady state growth rates. Ground based tasks of designing, fabricating and testing of the ampoule at GTE Laboratories have been completed. The ampoule is to be enclosed in a molybdenum cartridge as an added safety level of containment. The ampoule/cartridge assembly has been designed, fabricated and is currently being tested in the Ground Control Experiment Laboratory (GCEL). The GCEL contains a ground based equivalent of the flight unit, which is currently being certified for flight operations.

Double Diffusive Convection during Growth of Lead Bromide Crystals in Space

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Objectives: The objectives of the present program are to use microgravity environment to minimize thermo-solutal convection, significantly reduce the optical and acoustic scattering normally caused by convection, demonstrate lead bromide acousto-optic crystals with unparalleled optical perfection for advanced device application, and provide basic data on convective behavior in crystals grown by commercially important Bridgman process.

Lead bromide is a highly attractive material for the acoustooptic devices. Purification processes have been developed which permit physically sound and optically clear crystals to be grown. However, in common with many halide crystals, cutting, polishing and device fabrication can cause crystal damage. Hardening of the crystal by dilute doping has been suggested but uniform bulk doping for which the resulting crystal is optically homogeneous, is difficult to achieve in normal gravity. The aim of the present program is to test this hypothesis in normal and reduce gravity and to relate the results to the growth of device grade crystals.

Research Task Description: Lead bromide system is optically transparent in the visible range and it is an excellent model for Bridgman system permitting realtime visualization of the growing solid liquid interface. Also, we have shown that doping of lead bromide by silver improves the properties needed for fabrication significantly. In spite of success in growing cm size crystals, striations are commonly observed in doped halides. These striations are an indications of refractive index variations and hence homogeneity in the bulk of crystal. Even in the pure crystals, thermal convection can cause radial and longitudinal inhomogeneity. However, in the present case interaction of the thermal convection with solutal field of the doped material may also occur. This can create much more complex situation. For this reason we are studying the convection related growth parameters during crystal growth in 1-g and microgravity environment.

The task elements involve a set of crystal growth experiments using pure lead bromide and variable aspect ratios (r/L) in a two zone furnace. Here r is the radius of growth tube and L is the length of melt column. The variation of Rayleigh number (convection) for the onset of temperature oscillations will be studied as function of r/L . Measurements of the temperature distributions in growth tube will be made and time phase correlation of temperature oscillations will be studied to infer whether unicellular or multicellular flow exist. These data are important to understand the effect of heat flows on the oscillatory instability without solute effects. Similar experiments will be carried out employing doped lead bromide to evaluate the effect of varying the critical Rayleigh number ($Ra + Rs$) on the onset of temperature oscillations. Effect of these varying convection conditions on crystal quality will be evaluated. The data will be base-line and will be compared with the data obtained for crystals grown in microgravity environment.

Two sets of experiments were carried out: (a) to study the thermal convection (b) to study the solutal convection. Since lead bromide crystals are very anisotropic, all the crystals were grown in [010] direction in vertical Bridgman furnace by using prefabricated seed. This orientation is preferred by the optical physicists for the devices. The temperature profile for the crystal growth was kept identical. To change the magnitude of Ra and Rs aspect ratio and concentrations of dopants were varied. These boundary conditions imply that any observed change in the quality of the crystals should be due to thermal and solutal convection. Numerical computations were done for this system by Coriell (NIST)

to estimate critical concentration of dopant for the desired growth parameters. The characterization of crystals was carried out to estimate optical homogeneity by examining bulk transparency, birefringence, scattering and acoustic attenuation. Based on these studies, a microgravity experiment is planned for the growth of doped lead bromide crystal.

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Vapor Crystal Growth of Mercuric Iodide

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H-11280D

Objectives: Single crystals of mercuric iodide are used in high-efficiency x-ray and gamma ray detectors operating at ambient temperature. Optimal operation of the devices is determined to a large degree by the density of structural defects in the single crystalline material. Since there are strong indications that the quality of the materials is degraded by the effects of gravity during the growth process, a program was initiated to grow one or more crystals of mercuric iodide in the reduced gravity environment of space.

Specifically, there are two reasons to perform the space experiments:

1. Single crystals of mercuric iodide are prone to slippage under the effect of gravity, especially at the elevated growth temperatures, with a concurrent decrease in structural quality.
2. It is not clear what effects convection flows in the vapor phase have on the growth rate and the homogeneity of the crystals. Growth in reduced gravity would provide information regarding these questions.

Research Task Description: The first experiment, performed during the flight of Spacelab 3 (1985), was highly successful in the sense that all scientific objectives were fulfilled. The structure of the space-grown crystal was more homogeneous and the critical electronic properties were increased by a factor of seven compared with the best earth-grown crystals.

Preparations are under way for the next experiment, to be flown on the first flight of the International Microgravity Laboratory (IML). Present groundbased research and experiment development activities concentrate on improving the control system of the flight equipment and increasing the temperature of the growth process so that the larger crystals can be obtained in the limited time available during the flight.

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Vapor Growth of Alloy-Type Semiconductor Crystals

Rensselaer Polytechnic Institute
Professor Heribert Wiedemeier
NAS8-32936 (October 1989-March 1990)
NAS8-38143 (March-October 1990)
(NASA Contact: D.A. Schaefer; L. Jeter, MSFC)

Objectives: The present effort is part of a continuing research program directed towards the investigation of basic vapor transport phenomena and of crystal growth properties of electronic materials. The primary objectives of ground-based studies are the development and definition of optimum experimental parameters for flight experiments. The specific experiments to be performed in a microgravity environment include the investigation of vapor transport and crystal growth phenomena of the $\text{Hg}_{1-x}\text{Cd}_x\text{Te-HgI}_2$ system. Emphasis for this system is on the mass flux, on the unseeded and seeded growth of bulk crystals, and on the growth of epitaxial layers. The above experiments are performed in closed, fused silica ampoules.

The objectives of the $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ experiments are to determine the positive effects of microgravity on vapor phase crystal growth of ternary, alloy-type materials in terms of chemical and structural microhomogeneity, and of electrical properties of crystals grown in space. In order to achieve these goals it is necessary to perform corresponding crystal growth studies on ground which will serve as a comparative basis for the, meaningful analysis of microgravity effects. Thus, the objectives of ground-based studies are to determine the effects of gravity-driven convection on mass transport rates and on crystal morphology for the bulk and epitaxial growth of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ crystals. These objectives include the thermodynamic and fluid dynamic analysis of the mass transport processes, and the characterization of grown crystals in terms of defects and of electrical properties. The ultimate goal is a quantitative correlation between crystal morphology, electrical properties, and growth parameters for this system.

Research Task Description: Earlier studies demonstrated the effects of gravity-driven convection on mass flux and morphology of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ bulk crystals. The continued experimental tasks are directed towards the investigation of the effects of temperature profile and of the geometry of the condensation region of the ampoule on mass flux and crystal morphology. In addition, the effects of aspect ratio of the ampoule on the mass transport and crystal growth properties will be investigated. The ground-based tasks include the investigation of the above effects for different orientations of the density gradient with respect to the gravity vector, and for different transport agent (HgI_2) pressures and temperature profiles. The crystal characterization techniques include various microscopic and x-ray diffraction methods, chemical etching, and electrical measurements. The ground-based studies are designed to optimize experimental parameters for future flight experiments.

The major tasks of ground-based studies of the epitaxial growth of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ layers by chemical vapor transport reactions involve systematic investigations of the growth rate, morphology, homogeneity, and electrical properties of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ layers. These studies include measurements of the effects of substrate orientation relative to the density gradient, of temperature profile effects, and of transport agent pressure on the above properties. They are performed under horizontal and vertical stabilizing conditions with the goal to observe the effects of convective interferences on layer morphology and properties. The results of on-going ground-based studies are continuously evaluated and are used for the systematic improvement of growth parameters with the important goal to define optimum experimental conditions for the microgravity experiments of this system.

In addition to the experimental tasks, theoretical efforts involve the quantitative thermodynamic analysis of the system under investigation, the computation of fluid dynamic parameters, and the consideration of other possible effects on fluid flow and crystal growth under vertical, stabilizing and microgravity conditions. An important aspect of the theoretical effort is the further development and improvement of transport models for diffusion limited mass transport of simple and of multi-component, multi-reaction vapor transport systems.

Progress to Date: Earlier accomplishments under this program include quantitative mass flux measurements and the analysis of crystal growth properties of bulk and layer-type crystals. These investigations demonstrate the effects of even minute fluid dynamic disturbances on the chemical and structural microhomogeneity of grown crystals.

More recently, dynamic microbalance techniques were employed, for the first time, to determine quantitatively the vapor pressure of Hg over $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ for different compositions within the homogeneity range. This work led to the direct in-situ determination of the Hg vacancy concentration and to the derivation of the enthalpy of vacancy formation for HgTe , $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$, and $\text{Hg}_{0.6}\text{Cd}_{0.4}\text{Te}$. In addition, the pressure-temperature phase diagrams of the above systems were established based on these measurements. This work is being extended to related systems. These results provide valuable information for the further elucidation of the mechanism of vacancy formation of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$. Based on our development of a thermodynamic model for the $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ - HgI_2 vapor transport system, theoretical predictions of the mass transport rates and crystal compositions of this system are in good agreement with experimental observations for different pressures, temperatures, and a wide range of compositions.

In view of the limited time available for crystal growth on the USML-1 Mission, on-going experimental efforts are focused on the optimization of mass fluxes and growth rates of $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$ bulk crystals and epitaxial layers. For this purpose, different source material compositions and transport agent pressures are employed. In case of the bulk growth, "self-seeding" techniques are used in order to minimize multi-nucleation. For the control of the composition of the epitaxial layers of $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$, the post-growth cool-down procedures are very important. With respect to the morphology of the epitaxial layers, the crystallographic orientation of the CdTe substrate is very influential. The results to date of on-going studies show that the mass flux can be increased by an appropriate choice of source composition and transport agent pressure. The composition of the epitaxial layers is strongly affected by the combination of source composition and transport agent pressure. The morphology of the epitaxial layers is considerably different for different crystallographic orientations of the CdTe substrate.

The above theoretical and experimental results are of immediate practical value for the optimization of transport and growth conditions for the flight experiments of this system. In addition, the results of this work are generally applicable for the vapor phase crystal growth of ternary, alloy-type materials. Our predictive capability is of technological significance for the design, performance, and evaluation of vapor phase crystal growth on earth and in microgravity environment.

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2. SOLIDIFICATION OF METALS, ALLOYS, AND COMPOSITES

In-Situ Monitoring of Crystal Growth Using MEPHISTO

University of Florida
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(NASA Contact: Henri DeGroh, LeRC)
January 1, 1990 to January 1, 1991

Objectives: The proposed experiments are to be performed to gain a detailed understanding of the role of gravity driven convection during growth of faceted crystals. The scope of the investigation is defined such as to include the study of both the kinetics (i.e. the interfacial temperature vs. the interface velocity relationships) and the morphological (i.e. the threshold and size of interface instabilities and the resulting microstructures) aspects of solidification of faceted materials.

Research Task Description: A key aspect of the investigation is the use of non-invasive, direct, and real-time monitoring of the s/l interface temperature as well as the demarcation of the interface shape during growth. This is achieved by using the Seebeck and Peltier techniques and an experimental configuration by which two constrained s/l interfaces are created in a cylindrical sample such that a central column of liquid is enclosed by a column of solid at each end.

Under static conditions (i.e. when the interfaces are stationary), both the interfaces are at T_m . However, when one of the interfaces is set in motion, its temperature deviates from the equilibrium value (interfacial undercooling), with the magnitude of the undercooling being dependent upon the imposed growth rate and the atomistics of the growth processes. The morphology of the moving interface is controlled by the local growth conditions such as the thermal and solutal fields and convective instabilities.

As mentioned above, for both the kinetic analysis and the detection of morphological instability (e.g. a transition from planar to cellular) of the moving interface, the Seebeck thermoelectric effect is used: because of the difference in the Seebeck coefficients of the solid and the liquid, a temperature difference between the two s/l interfaces (one stationary, the other moving) generates a proportional EMF which can be measured externally and non-intrusively. Using this approach, the atomistics of the interfacial processes (e.g. dislocation free vs dislocation-assisted growth) can be deduced from an analysis of the interface velocity vs. interface temperature relationship. For the morphological analysis, the Seebeck signal again provides a detection tool for the onset of instability, while the interface shape can be delineated by current pulsing, making use of the Peltier effect. Simultaneously, the growth rate is measured by monitoring the change in the resistivity of the sample as a function of time. Correlations between the interface shape, microstructural morphology, microsegregation, and the growth rate are then used to deduce the effect of thermosolutal convection.

Experiments under carefully controlled and fully instrumented conditions are needed for such measurements. In this program, pure Bi and dilute Bi-Sn alloys (both of which exhibit a highly facet forming tendency) are being used as model systems to generate an extensive database for growth under 1-g conditions, in order (i) to define the most pertinent conditions for experiments in μ -g environment and (ii) subsequently for comparison with the μ -g results.

An integral part of the program is the extensive collaboration with the French MEPHISTO team, for both the ground based and the space-based experiments. As part of the collaboration, the various scientific, technical, and engineering aspects of the investigation are being addressed concurrently at the University of Florida and at CENG (Grenoble) and CNES (Toulouse). As part of an agreement with NASA, the MEPHISTO hardware will be flown on USMP-1 to carry out experiments on Sn-Bi alloys. The complementary Bi-Sn experiments are planned for the second flight of MEPHISTO on USMP-2.

Progress To Date: During the First year of the project, comprehensive literature survey of the thermophysical properties of Bi and Bi-Sn alloys has been carried out. The measurement of the Seebeck coefficients and resistivity of liquid and solid Bi as a function of temperature has been completed. Based on these measurements, the Seebeck EMF generated at the s/l interface is $45.6 \mu\text{V}/^\circ\text{C}$, which compares favorably with Ga ($1.8 - 2.2 \mu\text{V}/^\circ\text{C}$,³ used for a similar study).

This suggests that for Bi and Bi-Sn alloys, the Seebeck technique is especially suited for the measurement of interface temperatures. The measurement of the Seebeck coefficients and resistivity of dilute solid and liquid Bi-Sn alloys as a function of temperature and composition has been initiated. An experimental setup for carrying out fully instrumented runs is nearing completion. Also, procedures for the feedstock preparation and directional solidification of 100 cm long samples contained in quartz tubes have been finalized. Other technical/engineering/metallurgical issues being addressed include a study of graphite/Bi interactions (since graphite coated quartz tubes may be required for reduced friction), compensation of the volume changes in the sample by use of spring loaded ends and/or use of controlled porosity coatings, and the integrity of the quartz tubes during repeated thermal cycling.

Accurate determination of the Bi side of the Bi-Sn phase diagram has been undertaken together with an analysis of the effect of cooling rate on microstructural morphology as a function of composition. Preliminary experiments indicate that Bi has a high tendency to supercool prior to solidification, implying that the interfacial supercooling will be well within the detection limits of the Seebeck technique.

Extensive collaboration with the French MEPHISTO team has resulted in a detailed definition of the various scientific/technical/engineering aspects of the program. As part of the collaboration, cylindrical specimens 100 cm in length have been supplied for testing on the MEPHISTO engineering model. In addition, extensive tests of Bi and Bi-Sn alloys will be carried out in France in May-June 1991, using samples made at the University of Florida. According to the current timeline, the matrix of experimental conditions for MEPHISTO on USMP-2 will be defined in September 1991. Also as a part of the program, S.R. Coriell (Co-P.I.) of NIST is carrying out convective flow modelling for the Bi-Sn alloys.

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Alloy Undercooling Experiments in Microgravity Environment

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NAG8-826 NASA Contact: R. C. Darty, MSFC)
May 19, 1989-October 18, 1990

Objectives: The objectives of this research are (1) to evaluate containerless melting and solidification of nickel and iron base alloys with and without softened glass coatings; (2) to develop techniques for the study of recalescence and growth behavior during solidification of undercooled alloy melts in microgravity; (3) to develop an understanding of undercooling phenomena in microgravity; and (4) to develop an understanding of the microstructures so produced.

Experimental techniques are being defined and documented for performing and analyzing undercooling experiments in space and on the ground. The scientific aim of the current modeling and experimental studies is to obtain baseline data and a baseline understanding of nucleation, growth, solidification, and structure of highly undercooled alloys on which comparable experiments will be conducted in space.

Research Task Description: The first alloy undercooling experiment in a microgravity environment was performed during the Columbia STS 61-C mission in January 1986. The results of the flight experiment have been published. Presently, science requirements are being defined and documented for a series of alloy undercooling experiments aboard IML-2 using TEMPUS hardware. The directly related ground-based experimental and analytical studies include thermal history measurements during the rapid recalescence and solidification of undercooled alloys, dendrite growth rate measurements, metallographic studies, and modeling of dendrite growth in alloy melts. Results of NASA sponsored work at MIT on solidification of undercooled alloys have been reported in about thirty published papers.

Progress to Date: Undercooling experiments have been performed using Ni-Sn, Fe-Ni, and Fementalloy alloys. New techniques have been developed for the study of undercooled melts in containerless Processing. A system for induction melting and solidification of iron and nickel base alloys coated with softened glass with simultaneous temperature measurement has been developed. High-speed cinematography has been utilized to observe the solidification of undercooled Ni-25%Sn alloy. Reheating curves measured during recalescence have been used to obtain dendrite tip velocity, fraction solid after recalescence, and other solidification features. Microstructure and microanalysis of samples produced were related to thermal and cinematographic results.

Recent work has emphasized techniques for levitation melting of droplets without softened glass coatings, for interrupted solidification studies, and for videotaping surfaces of samples during undercooling, recalescence, and final solidification.

The thermal data, video, and cinematographic data have provided direct insight into the mechanism of solidification of undercooled metal alloys and have led to the development of a detailed model of growth of alloy dendrites in undercooled melts. Measurements of dendrite tip velocity showed good agreement with predictions based on recent theories of steady state free dendritic growth. The maximum recalescence temperature has been found to be the temperature predicted by an adiabatic thermal balance combined with the equilibrium lever rule. Recalescence times have been found to decrease rapidly with increasing undercooling, and total solidification times have been found to decrease with increasing undercooling. Dendritic growth in undercooled melts can occur with a unique morphology of the growth front which has been described in the publications. The majority of the dendrite arms disappear during coarsening. The

dendrite morphology undergoes a gradual and continuous microstructural transition with increasing undercooling. Regardless of morphology, the microstructure becomes finer with increasing undercooling. A detailed and comprehensive model is being developed for processes occurring behind the dendrite tips during recalescence and subsequent solidification.

Experimental work on Fe-Ni alloys (5%, 10%, and 30% Ni) has confirmed the growth models developed from observations of the Ni-Sn system. Fe-Ni alloys are being studied, in part, because of the narrow equilibrium solidification range. At high undercoolings dendrite growth velocities are very high and nonequilibrium solute partitioning is an important consideration. In addition, in the Fe-Ni peritectic system a double recalescence phenomenon has been observed in alloys that normally would solidify with FCC austenite as the primary phase. Apparently, BCC delta ferrite nucleates preferentially, and the austenite nucleates after recalescence of the metastable delta phase.

Experiments have been performed with Fe-B, Fe-P, and Fe-Si alloys. These alloys are interesting because of their glass-forming ability, because of their very low partition ratios, and because of their wide freezing ranges. Observed dendrite growth velocities in these alloys have been measured, and are observed to be much slower than in the iron and nickel base alloys studied earlier. Recalescence times are one to three orders of magnitude slower. These alloys provide the potential for substantially increasing our understanding of dendritic and nonequilibrium solidification of undercooled alloys. Detailed experimental data on recalescence in undercooled FeP alloys have been compared with recent theories of dendrite growth under conditions of nonequilibrium solute partitioning at the dendrite tips. Good evidence is found for a shift from equilibrium to nonequilibrium partitioning as the undercooling increases.

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Kinetics of Diffusional Droplet Growth in a Liquid/Liquid Two Phase System

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In-House

Objectives: The Chemistry and Polymeric Materials Branch conducts experimental and theoretical research to advance the science and technology of organic and polymeric materials having applications as optical and other technologically important devices. Studies relate to gravitational influences on solidification, crystal growth, thin film growth, and polymerization of such materials appropriate for study.

Research Task Description: Space laboratories in free fall, offer an environment in which body forces on fluids can be minimized over a relatively extended period of time and range of experimental conditions. Some advantages are to provide a quiescent environment to allow growth of more defect-free crystals, and solidification of more finely dispersed composites in low viscosity fluids by reducing buoyancy-driven convection and sedimentation. These effects are important, for example, in the study of factors yielding poor dispersions in miscibility-gap type system. A fundamental understanding of coarsening mechanisms, possible in low gravity experimentation, can lead to further understanding of factors contributing to fatigue in metal alloys, instability in foams, behavior of fogs and aerosols, and generally almost any of the multi-phase systems which cover a broad range of technologies. One such coarsening mechanism is Ostwald ripening. This is the process by which larger droplets grow at the expense of smaller ones by diffusion of mass away from droplets below a critical radius toward ones above this size. This branch is leading a research program funded to perform a flight experiment which will give data on the ripening process where gravity effects have been virtually eliminated. This experiment is designed to increase understanding of the fundamental phenomenon of diffusional grain/droplet growth.

Another research goal is to grow high quality thin films and single crystals of nonlinear optical organic materials in low-gravity by vapor transport, melt, and solution processes. Organic materials are of interest for use in all optical communication and signal processing systems because their nonlinearities are orders of magnitude larger than those of conventional inorganic materials. Additionally, organic materials offer flexibility of molecular design and a high damage resistance to optical radiation. They promise an unlimited number of crystalline structures, allowing optimization of device performance. Consequently, these materials might make it possible to replace electronic switching circuits in computing and telecommunication systems by purely optical devices. Microgravity should contribute to processing of high quality films and large single crystals of organic compounds, with optimum nonlinearities, nearly impossible on Earth due to convection.

Another branch activity related to droplet coarsening is examination of kinetics of the coarsening process due to droplet coalescence in an immiscible liquid-liquid dispersion in the absence and in the presence of gravity. The individual and collective roles of Brownian motion, Marangoni migration, and sedimentation on promoting coalescence. Current work is all ground-based with projected efforts toward establishing a flight experiment.

There is currently a feasibility study to apply Monodisperse Latex Reactor (MLR) technology to spherical dye-laser research. This activity has already successfully resulted in the insertion of fluorescent dyes into polystyrene spheres.

Progress to Date: We have proposed and received approval to perform a flight experiment to study Ostwald ripening in a liquid-liquid system. To date, engineering assessments have begun to mate science

requirements with potential flight hardware. Laboratory hardware is very nearly complete for some ground-based testing.

We have received headquarters approval to begin ground-based studies on organic crystal and thin-film growth for nonlinear optical applications. This past year, there have been several presentations on this topic, specifically, by Dr. Craig Moore. Two articles have been accepted for publication: Craig E. Moore, and Beatriz H. Cardelino, "Static Second-Order Polarizabilities of Amino-and Nitro-Benzophenones", to be published in the Journal of Molecular Structure; and, B. Penn, B. Cardelino, C. Moore, A. Shields, and D. Frazier, "Growth of Bulk Single Crystals of Organic Materials for Nonlinear Optical Devices: An Overview" to be published in Prog. Crys. Growth and Characterization. Other submissions are in progress, and several presentations scheduled for 1991. University relationships have been established to perform synthesis of unique compounds through the Joint Venture (JOVE) initiative and the Historically Black Colleges and Universities (HBCU) program. Theoretical screening and crystal characterization techniques have been established at HBCUs. With the new funding, build-up of in-house synthesis and characterization capabilities have begun.

Several papers have been published over the past two years with regard to separation processes in miscibility-gap type systems. Particularly, two papers, one in *Thermochimica Acta* (1989), and the other in the *Journal of Crystal Growth* (1990), provide strong evidence for the role of surfaces during solidification to produce monotectic alloys. These experiments are consistent with the gradient theory put forth by H.T. Davis.

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Gravitational Effects on Liquid Phase Sintering

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Professor Randall M. German

Professor Krishna Rajan

Professor David Knorr

Objective: This research deals with the role of gravity on both the macrostructural and microstructural changes in powder compacts during liquid phase sintering. A classic form of liquid phase sintering is observed in the heavy alloy tungsten-nickel-iron system, where mixed powders produce a liquid at temperatures over 1465°C. When tungsten heavy alloys with less than approximately 83% W are processed on earth there is solid-liquid segregation, leading to shape loss, compositional gradients, microstructural gradients, and property gradients. Microgravity experiments provide an opportunity to study liquid phase sintering without the disruptive effects associated with gravity. At the macrostructural level, distortion and segregation are studied versus alloy composition, processing pathway, and basic system thermodynamic parameters. These results indicate the causes of compact distortion, allowing models that predict the severity of distortion, indicating possible tooling corrections to compensate for distortion. At the microstructural level, the research is isolating the gravitational contribution to grain coarsening from coalescence in high solid content alloys. The solid grains segregate at the bottom of the compact during ground-based sintering, leading to differential rates of grain growth and pronounced density, grain size, connectivity, and contiguity gradients. The theories for grain growth can not be tested in ground-based experiments because of settling. Likewise, the materials processed on earth are not treated by current theories for grain growth by solution-precipitation, because of significant grain contact and coalescence.

Research Task Description: The research tasks involve the fabrication and assessment of various tungsten heavy alloy compacts that are sintering to induce various degrees of slumping and segregation. Measurements are made on distortion, settling, viscosity, grain size, contiguity, and connectivity versus the independent variables. Observations on grain coalescence and rotation are being aided by electron channeling and x-ray texture measurements.

Progress to Date: The progress to date includes design of critical flight experiments that will involve seven samples and three sintering times. Further work has defined the shape accommodation thermodynamics for liquid phase sintered materials, the kinetics of grain rotation and coalescence, and determined the experimental limit for avoiding liquid-solid separation in earth-based sintering. This value depends on the density difference between the two phases (solid and liquid). Experiments have been completed to show the degree of segregation versus liquid content and sintering time. Models have been constructed for solid-liquid separation and coalescence induced grain growth. A significant finding is that coalescence is a contributor to coarsening in liquid phase sintering. A modified grain growth equation has been developed that includes the system contiguity. Finally, a distortion model has been generated based on viscous flow of the solid-liquid mixture under gravity and this model matches well with two sets of experimental distortion experiments.

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Isothermal Dendritic Growth Experiment

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NAS3-25368 (NASA Contact: E. Winsa, LeRC)

Objectives: To perform Isothermal Dendritic Growth Experiments (IDGE) during Shuttle spaceflight on a well-characterized, pure, molten, material under microgravity conditions. Data from spaceflight will be used to test critically competing theories of diffusion-controlled, convection-free dendritic growth.

Research Task Description: The Principal Investigator has over the past ten years developed special methods for preparing in ultra-pure states succinonitrile, $\text{CN}-(\text{CH}_2)_2\text{-NC}$, a transparent organic material that solidifies as a body-centered-cubic crystal, with less than 1 ppm total impurity content. Careful ground-based studies have shown that when supercooled succinonitrile is crystallized, dendritic crystals develop and grow under the simultaneous heat transport conditions provided by *thermal conduction* and *thermal convection*. Convection arises from the thermal gradients surrounding the growing dendrites which, in turn, alters the local density of the adjacent melt. In the presence of earth's normal gravitational acceleration, such density alterations lead to fluid motions called convection, which either enhance or diminish heat flow. Since dendritic growth is an especially simple example of natural pattern formation--observed commonly in most cast alloys--it assumes a significance both of theoretical and practical interest. Theories of dendritic growth purport to allow prediction of dendritic morphologies and growth rates under specified supercooling conditions. To test the accuracy and reliability of such theories, dendritic growth must be observed under the most stringent conditions. Specifically, the supercooling and transport conditions must be known precisely. The former becomes straightforward if the purity of the test material is very high--usually below 1ppm total impurity content. The latter becomes possible only if the molten phase remains static during crystallization. Efforts to achieve the conditions of a static, *i.e.*, convection-free melt require that either the melt's viscosity remains high, or that the gravitational body force remains small. Efforts to achieve one or the other of these requirements have shown that the only practical method involves reducing the gravitational acceleration to the micro-g level. This will be accomplished by the IDGE spaceflight.

Progress to date: The P.I. and NASA, through its Lewis Research Center, have been developing the IDGE for four years, passing from the science requirements to the critical design phase in a sequence of science and engineering development tasks. At present, prototypical hardware has been developed and initially tested, which will allow the IDGE to be flown as a semi-autonomous flight package aboard the USMP. During 1990, the P.I. and his team have concentrated on developing the first modification of the IDGE crystallization chamber--a key flight hardware component--that contains the succinonitrile sample, along with means to nucleate it, to measure the internal temperatures, to assess *in situ* its purity, and to observe and measure the growth rate, supercooling, tip radius, and side-branch spacings. Tests have shown, to date, that succinonitrile can be stored for lengthy periods (over one year) in the IDGE flight chamber without significant amounts of contamination. Moreover, the use of thermoelectric cooling to induce nucleation and subsequent dendritic growth has proven successful in recent integrated IDGE tests performed by NASA with high-fidelity prototypes of the flight style thermostat. Finally, we have also worked on assessing the scientific validity of the IDGE optical data, taken in the ground test program with the new growth chamber. These tests are still under evaluation, but preliminary indications are that suitable measurements of dendritic growth kinetics and morphology can be extracted from the IDGE optical data.

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Thermophysical Properties of Metallic Glasses and Undercooled Alloys

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Grant No. NASA 496954MG3203550

Objectives: This project is aimed at studying the physical properties of undercooled metallic alloy melts which relate to glass formation. To accomplish this, we have proposed to develop calorimetric methods to investigate the specific heat and thermal conductivity of alloy melts both in the equilibrium and undercooled regime. The project includes use of conventional ground base measurements (differential scanning calorimetry) together with the development of a non contact calorimetry measurement on a liquid drop compatible with the microgravity environment of the TEMPUS electromagnetic positioning and heating hardware. The data obtained from these studies will be used in conjunction with a more general study of crystal nucleation kinetics in undercooled melts. In particular, we plan to investigate the degree to which refractory alloy melts can be undercooled. We will use the results of heat capacity measurements to determine the enthalpy and free energy functions of the undercooled melt, and will combine this with classical nucleation theory to develop a description of the nucleation kinetics and interfacial free energy between the melt and nucleating crystalline phases. Proposed alloy systems for study include the AuPbSb, AuGe, PdCuSi, NiZr, and Ni/Nb systems (in order of increasing melting temperatures).

The results of heat capacity measurements will also be used to experimentally determine the entropy of a liquid alloy as a function of temperature. By comparing this entropy function with that of the solid, the Kauzmann (and inverse Kauzmann) isentropic temperatures can be determined for solid/liquid equilibrium. The relationship of the Kauzmann temperature to the experimentally observed glass transition can then be assessed. It has been argued that the isentropic points for liquids and solids are associated with ultimate limits for undercooling and superheating. We plan to investigate this hypothesis.

Research Task Description: The project consists of two primary tasks. First, we will carry out a series of ground base calorimetry measurements on several liquid metallic alloys. Using a Setarim DSC 2000 and a Perkin Elmer DSC 4, we will determine the heat capacities of several glass forming eutectic alloys as a function of temperature in both the liquid and solid phases over the broadest range of temperatures experimentally achievable with this equipment. This includes measurements at lower temperatures performed with a modified DSC 4 operating in a liquid helium cooled cryostat. This low temperature data is essential for determining the total entropy function of solid phases. These experiments have already been carried out on a AuGe eutectic alloy for both the two phase solid and the liquid. We are particularly interested in the difference in heat capacities of the solid and liquid phases as a function of temperature. This difference directly gives the rate of change of the entropy difference between the solid and liquid phases. Ground base data are also available for AuPbSb alloys. These data have been used to critically evaluate the kinetics of crystallization in the undercooled alloy.

Our second task is to develop a non contact specific heat measurement for high melting point liquid alloys which could be carried out in a microgravity environment using the TEMPUS facility. A systematic study of possible methods has been carried out. It was concluded that an AC method would be most suitable. An experimental AC technique which employs the TEMPUS electromagnetic positioning device, non contact temperature measurement, and AC modulation of the power to the liquid drop has been developed. The experimental concept is described in detail in a recent publication. We are currently trying to work with the Dornier team to determine how best to implement this experiment on TEMPUS.

Finally, we are collaborating with the group of Eugene Trinh and Kinichi Ohsaka (of JPL) in their efforts to develop a ground base technique for measuring the total enthalpy function of an alloy melt. Ohsaka is currently utilizing an electromagnetic levitation system in our laboratory together with non contact temperature measurement hardware developed at JPL.

Progress to Date: We have completed a detailed study of the crystallization kinetics in undercooled melts of the AuPbSb system. Measurements of the specific heat of the undercooled alloy were used to compute the entropy and free energy difference between the undercooled liquid and crystalline phases. These results represent the most systematic study to date of the thermodynamic functions of a metallic glass forming liquid. The data in turn were used as direct input in an analysis of the nucleation kinetics of crystalline phases. We have also carried out measurements of the heat capacity of the solid and liquid phases of the eutectic alloy in the AuGe system using our Perkin Elmer DSC 4 apparatus. We have measured the heat capacity of both the solid and liquid phases as a function of temperature. Data for the liquid phase have been obtained for undercoolings up to 100 C. We have computed the entropy function for both phases and obtained an estimate of the Kauzmann temperature for the eutectic alloy. We have found that liquid alloys have both an excess negative enthalpy of mixing and excess heat capacity with respect to the two phase solid alloy.

We have completed a developmental study of an AC non contact calorimetry measurement to be carried out on TEMPUS. The experiment is outlined in publication No. 4. The experiment employs the electromagnetic heating and positioning capability of TEMPUS. Further it exploits the non contact temperature measurement capability of TEMPUS. The AC method involves direct measurement of the AC temperature excursions of a liquid drop subject to an AC modulation in input power. The external relaxation of the drop temperature by radiation, the internal thermal relaxation of the drop, and other factors have been taken into account in designing an experiment. It has been found that heat capacity measurements with accuracy of a few percent are feasible on liquid drop of radius of order 1 cm at temperatures in the range from 1000 C to 2000 C. These conditions require an AC experiment at frequencies in the range of 0.1 Hz. In order to obtain absolute values of the heat capacity, it will also be necessary to determine the absolute power input to the drop as a function of its steady state temperature. One approach involves measuring the total hemispherical emissivity of the liquid drop as a function of temperature. Methods of accomplishing this are currently under evaluation. A blackbody balometer has been examined as one possibility. Finally, as an added feature of the proposed experiment, one can determine the temperature dependent thermal conductivity of the liquid alloy. When the period of the power modulation is comparable to the internal thermal relaxation time of the drop, the AC temperature excursions of the sample surface become frequency dependent. This frequency dependence can be analyzed to obtain the internal relaxation time of the drop. Under suitable conditions, this in turn can be used to determine the thermal conductivity of the liquid alloy. As such, our proposed experiment yields both heat capacity and thermal conductivity data.

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Casting and Solidification Technology (CAST)

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Ronald Porter
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NAS8-37292 (NASA Contact: R. C. Ruff, MSFC)
December 1986 - December 1990

Objectives: The objectives of research are: (1) to determine the influence of gravity on the fluid flow and nucleation that occurs during casting, and (2) to investigate the solidification and coarsening processes of dendrite arms and their subsequent influence on the grain structure in castings.

Research Task Description: The purpose of the investigation is to study the directional solidification of metal-model materials under low-gravity conditions. In particular, the inverted density layer and the thermal and solutal fields ahead of growing a interface will be analyzed. This investigation is an extension of previous low-g studies done on Space Processing Applications Rocket (SPAR) and KC-135 flights. To complete these studies, longer periods of low-g are required in order to allow solidification to occur at slower and more controllable rates. Therefore detailed analysis will be made of fluid motion near the solidification interfaces using the optical techniques (Schlieren, shadowgraph, interferometry and holography) available in the ground based laboratory and in the Fluid Experiment System on IML-1. To aid in separating the thermal and solutal profiles, thermocouples will be placed at intermittent locations along the cuvette wall. The temperature measurements will enable the investigators to mathematically separate the thermal and solutal effects on the interferograms.

Progress to Date: Two optics systems were assembled. One that provided confocal processing and particle tracking capabilities and a second interferometric system. The onset of convective instabilities within the inverted layer and concentration and temperature fields are being documented with this apparatus. A cuvette design that would accommodate shrinkage and expansion of the fluid was completed. An instrumented cuvette was assembled and operated under typical solidification conditions. Comparisons of concentration and temperature fields were made with optical and analytical predictions. A KC-135 flight rig was assembled incorporating a confocal optical system and VCR data recording. The advanced fluid thermal model has progressed continually and a graphics capability has been added so the solidification process can be viewed in real time as it is being calculated. Ground Control Runs have been completed on the FES hardware. The PI's are presently performing science runs in the holographic Ground System.

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3. FLUIDS, INTERFACES, AND TRANSPORT

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Dr. R. Glynn Holt
JPL Contract No. 958722
January 1, 1989 - June 15, 1993

Objectives: The goals of this research are: (1) to determine the rheological properties of liquid drops in the presence or absence of surface active materials by exciting single drops into their quadrupole resonance and observing their free decay. The resulting data coupled with appropriate theory should enable us to understand better the physics of the underlying phenomena, providing a better foundation than earlier empirical results could; and (2) to investigate the mechanisms for coalescence of droplets with and without surfactants using a variety of techniques for perturbation of the interface between the drops. In addition to providing valuable physical insight into the coalescence process, practical knowledge in the form of determination of an energy-efficient approach to enhancing drop coalescence will be gained.

Research Task Description: The means by which we hope to achieve the aforementioned goals can be divided into two classes of effort: (1) ground-based efforts, both theoretical and experimental; and (2) microgravity experiments, to be performed on the inaugural flight of the Drop Physics Module on USML-1, scheduled for May, 1991. Our work thus far has centered on the ground-based experiments, as the results of such experiments will serve to guide and define the experiments on the DPM on USML-1. All of the tasks involve, both implicitly and explicitly, the interaction of liquid drops with acoustic fields. This interaction provides a containerless method for studying surface properties non-invasively, as well as (via resonant interactions with the shape modes of spherical drops) information about drop dynamics and interfacial properties for a time-dependent system.

Progress to Date:

I. Ground-based efforts

Single-axis levitation

The first project we will discuss is the single-axis levitation effort. We took as our model a well-known system, and proceeded to purchase, assemble and build the necessary components. The heart of the system is an exponential horn transducer driven in its fundamental longitudinal resonance mode. A reflector (with a PZT sensor disk is mounted in its face) is placed an appropriate distance away to create a standing wave field in the air gap between the transducer and reflector, fine-tunable via micropositioner mount.

Liquid drops are levitated and excited by applying a time-varying voltage signal to the transducer. This consists of the sum of the levitation voltage V_L (a sine wave tuned to the longitudinal resonance frequency of the transducer) and a modulated carrier voltage $V_m V_c$, where V_c is sinusoidal with the frequency of one of the harmonics of the transducer, and V_m is varied over the frequency range corresponding to typical resonance frequencies for various shape oscillation modes (we use primarily the quadrupole mode) of the drop in question. To compare with earlier results, the oscillations of drops of a range of sizes have been observed using an optical scattering technique developed. The voltage output of a photodiode positioned on the optical axis defined by the light source and the drop center is digitized, stored and analyzed on our microcomputer.

Experimental results obtained thus far include: (1) power-law dependence of the quadrupole resonance frequency f on the size d of the drop, $f \propto d^{-3/2}$; (2) the variation of quadrupole resonance frequency with aspect ratio. The strength of the levitation field was successively increased in order to flatten the drop while the determination of the quadrupole resonance frequency was obtained for various drop sizes. The decrease in frequency with increasing aspect ratio is predicted by Subramanyam, and observed in; and measurements of drops with surfactants of varying concentrations showing the variation of frequency and damping with surfactant concentration, data for which we hope to obtain theoretical estimates for comparison.

Triple-axis levitation (DPM simulator)

To augment our understanding of the practical problems of positioning and manipulation in the DPM, JPL has provided our lab with a resonant acoustic chamber and four drivers. This system is capable of producing a fully controllable three-dimensional (hence "triple-axis") acoustic field. With such a device, we can mimic the positioning characteristics of the Near-Ambient Chamber (NAC) exactly (to scale, of course), by using styrofoam spheres as sample levitation objects. In addition to simply "getting a feel" for 3-D levitation, we have designed a scheme by which we can deploy, position, and bring together two samples in the chamber with a minimum relative velocity, facilitating our study of drop coalescence in air. The generation of the driver signals with the appropriate frequencies and phases, and the monitoring of the chamber pressure for feedback purposes, is accomplished by a fully automated, software controlled system consisting of a microcomputer, A/D, D/A boards, plus external amplifiers.

Several schemes for deploying, translating, and "coalescing" two styrofoam samples using various combinations of mode-switching, gain and phase control have been successfully tested. These initial efforts were undertaken in a setup with a high degree of fidelity to the NAC. Because of this, smooth translation in the z-axis direction was not achieved, since the z-direction is also the direction of the gravitational force. Construction of a new chamber where translation can be attempted in a constant g-potential plane is currently underway. The software developed should provide JPL with an algorithmic basis for the macro sequences which will facilitate control of the dual drop coalescence experiments planned for USML-1.

Drop Coalescence

We are currently performing experimental studies in hopes of shedding light on the fundamental processes involved in the inception phase of coalescence. The experimental scheme involves acoustic levitation of two immiscible liquid drops (usually hexane) in another host liquid (usually water) by exciting a typically mixed-mode resonance of a quartz rectangular chamber. The nearly-neutral buoyancy of the drops allows us to use a relatively gentle acoustic field to position the drops, thereby reducing distortion of the samples, and minimizing unwanted streaming effects. High-speed photography has been used to investigate the dynamics of coalescence of pure and surfactant-coated drops, sometimes using a novel cavitation technique to induce coalescence in the surfactant-coated drops. Additionally, methods are being developed to probe the statistical nature of coalescence times.

Drop oscillation modelling

Theoretical efforts have begun towards solving the equations for shape oscillations of liquid drops in the air in the presence of varying concentrations of soluble surfactants. We will build on results obtained by Lu and Apfel [10] for liquid-liquid systems, with our ultimate goal being the formulation of an state equation description for the relationship of various surface properties with the

concentration of surfactant. Results in [10] indicate a complicated interplay between various properties (surface shear and dilatational viscosities, Gibb's elasticity) of the interface and the bulk properties of both liquids for determining mechanical motion which can be simplified when the host fluid is air, which will be possible for the flight experiments.

II. Flight experiment definition

Determination of the exact sequence of experiments, selection of the flight sample and surfactant materials, identification of sub-experiments which can be performed on the ground to verify ideas for flight -- in short, all the various effort involved in designing a SpaceLab experiment are being coordinated, and are fast approaching a final status as Functional Objectives for the USML-1 mission.

Summary

We have attempted in this presentation of technical results to indicate the bustle of activity here at our Yale labs surrounding this project. We feel confident that, based on our results so far, our DPM experiments will not only be feasible, but will represent valuable original contributions in the field of surface science. Likewise, the ground-based experiments, originally designed to support and define the DPM experiments, have expanded in new directions which will provide original results in such fields as nonlinear drop dynamics, emulsion technology, and of course surface science.

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Interfacial Phenomena in Multilayered Fluid Systems

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Professor Sedat Biringen
Professor R.L. Sani
Professor Charles Ward, University of Toronto

Objectives: The main objective of the proposed research is to investigate the flow structure of interface/surface tension gradient driven convection in a three immiscible liquid layer system, in this configuration one outer layer may be a gas. This topic applies to the encapsulated float zone, biological crystal growth, and to the Bridgman and Czochralski technique. The incentive for investigating the phenomena under microgravity conditions is that then the primary forces which induce convection are interfacial ones. One goal is to find criteria to suppress surface tension driven flow in the encapsulated electronic material melt in a low-g environment.

Research Task Description:

Experimental Efforts:

The main objective is to prepare a flight experiment for the IML-2 mission in 1994. The experiment is planned to be run on the Bubble, Drop, and Particle Unit developed by ESA.

(Koster:)

A light sheet technique and particle image velocimetry is used to measure flow patterns and local velocities. Holographic real time interferometry is used to evaluate temperature fields, and local thermocouples/RTDs are used to retrieve information about any time-dependent structure of the flow.

Test-cells of different geometries and end-wall boundary conditions are used for experimentation. Several experiments were performed in order to investigate the following issues: Heating differentially from the side, we investigate the single layer with a) water, b) FC-75, c) silicone oil and d) a double layer of FC75/water with negligible interface tension gradient to assess buoyancy effects. Each layer is about 1 cm high. The same experiment is repeated with silicone oil and water which does have a strong temperature dependence of the interface tension. The influence of the ratio of physical properties on fluid flow are of interest. Of particular interest is the influence of different values of interface tension on fluid physics.

(Ward:)

The primary contribution by Canada is in the correct choice of immiscible liquids. Thermophysical values (surface and interface tensions as a function of temperature) of different liquids are being measured by Dr. Ward at the University of Toronto. Dr. Ward will fly one or two KC135 flights, sponsored by CSA.

Numerical Efforts:

The objectives of the numerical efforts are to study stability and flow patterns of flow in multi-layered fluid systems subjected to temperature gradients either parallel to or perpendicular to the fluid interface with and without gravity effects.

(Biringen:)

Work emphasized the two-layer system, using full Navier Stokes equations. Production runs consider different Prandtl number ratios, fluid depth ratios, thermophysical property ratios, various and residual gravity effects. Additionally, the adequacy of the flat interface/surface assumption (90° contact angles) will be tested by allowing small interface/surface deformations through the imposition of a linearization of the deformable interface boundary conditions. Further, the capabilities of the numerical code will be extended to efficiently compute very high Prandtl number flows in one layer (to simulate glassy encapsulants).

International Participation

Besides the participation of Canada, this project is a collaborative effort between the PI and a group of ESA sponsored European scientists under the leadership of Dr. J.C. Legros at the University of Bruxelles. Here the main research topic is the investigation of the temperature gradient perpendicular to the interfaces. Dr. T. Doi, NASDA, participated for one year in this project, doing numerical analysis of the two-layer problem.

Publications

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Surface Tension Driven Convection

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Professor Y. Kamotani
NAG3-570 (NASA Contact: T.P. Jacobson, LeRC)
October 1989 - October 1990

Objective: The objective of the investigation is to design a thermocapillary experiment to study the transient and steady-state flows in the long-duration low-g environment of the Shuttle.

Research Task Description: The experiment consists of a circular container (5 cm dia. and 5 cm deep) filled with silicone oil, heating systems, and a data acquisition system. The fluid free surface will be heated locally by a CO₂ laser or by a submerged circular heater placed at the center. The resultant temperature variation along the free surface will generate thermocapillary flow in the container. The flow field will be studied by a flow visualization technique and the temperature distribution along the free surface, which is important because it determines the driving force of the flow, will be measured by a thermography technique. The surface heat flux distribution, the heating level, and the static free surface shape will be varied to study their effects on the nature and extent of the flows. Two series of experiments are planned. In the first one, the basic thermocapillary flow will be studied and attempts will be made to obtain oscillatory thermocapillary flow. In the second series the oscillation phenomenon will be studied in detail because it is considered to be an important aspect of thermocapillary flow. Ground-based and drop tower experiments together with a numerical analysis have been made to provide base data and to insure that the operating condition and the configuration will lead to flows that can be reasonably observed and measured.

Progress to Date: The fabrication and testing of the flight hardware of the experiment are being done at NASA/Lewis and the work is nearly completed. After systematic study the flow visualization technique has been finalized. At CWRU the study of oscillatory thermocapillary flow is being conducted using a small test cell. The onset conditions and the temperature and velocity fields during oscillations have been analyzed. Techniques to study the free surface motion during oscillations are being investigated. The scaling analysis of thermocapillary flow has been completed. It is being expanded to include the deformation of free surface.

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Presentations

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Thermocapillary Migration and Interactions of Bubbles and Drops

Clarkson University
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NAG 3 1122 (NASA Contact: M. Hill, LeRC)

Objective: The objective of this investigation is to make experimental measurements of the thermocapillary migration velocities and shapes of single and interacting gas bubbles and liquid drops under the action of an applied temperature gradient in low gravity.

Research Task Description: The above experiments are planned for conduct in the Bubble, Drop, and Particle Unit (BDPU) in orbit. The results will be compared with predictions from existing theory and new theoretical models to be developed as part of this research. The project is in the definition phase. The research task for the period involves performing tests on candidate systems and conducting feasibility studies.

Progress to Date: Candidate experiments were performed with air bubbles in silicone oils and methanol drops in silicone oils. Also, experiments were performed on the dissolution and growth of air bubbles in a silicone oil to assess the importance of size change effects. Order of magnitude calculations were made in establishing a preliminary test matrix. Contact was established with the appropriate personnel in Europe associated with the fabrication of the hardware.

Publications

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Measurement of the Viscosity of Undercooled Melts Under the Conditions of Microgravity and Supporting MHD Calculations

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Dr. O.J. Ilegbusi
Elliot Schwartz
NAG8-815 (NASA Contact: R.C. Darty, MSFC)

Objectives: The objective of this research is to develop the mathematical framework for planning an in-flight experiment involving the electromagnetic heating and positioning of an undercooled metal sample under microgravity conditions. The relaxation of the sample after the application of a brief current pulse which will generate an inward electromagnetic force that will squeeze the sample will be observed. The sample will relax in an oscillatory mode, and by examining the rate at which the amplitude of the oscillations is decreased, the viscosity of the undercooled melt can be deduced. In addition to providing a unique way of determining the viscosity of undercooled metallic melts, the project will provide information to other investigators performing undercooling and calorimetry experiments using levitation melting.

Research Task Description: The current research pursues three directions: (1) extensive computational work is being carried out to determine the effect of different materials and sample size on the electromagnetic force field, velocity field, temperature field, and free surface shape; (2) examine the behavior of deformed samples under TEMPUS experimental conditions; and (3) modeling of the deformation kinetics, the rate at which a sample is deformed upon the sudden application of an electromagnetic force field and the subsequent relaxation process.

Progress to Date: Important milestones of the research include the following: (1) the development of a numerical method to calculate the electromagnetic force field and predict the equilibrium shape of the metallic specimens; (2) calculation of melt velocities and temperatures in levitation-melted specimens; and (3) calculation of what happens to the specimen, subject to both heating and positioning coils, when either the heating coil is switched off or when the current in the heating coil is reduced.

Publications

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Critical Fluid Thermal Equilibration

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Dr. R. F. Berg, NIST
Dr. M. R. Moldover, NIST
Dr. J. Straub, Technical University of Munich (FRG)

Objectives: This experiment will examine the thermal relaxation and the fluid density profile as a function of time after a temperature perturbation of sulfur hexafluoride (SF_6) near its liquid-vapor critical point in the low-gravity environment of the Shuttle. Past low-g critical fluid experiments yielded unexpected results which were perhaps due to unanticipated time scales for relaxation dynamics. Future critical fluid experiments will depend on achieving thermal equilibrium to within a specified tolerance and on knowing how phases develop or disappear. This work is intended to determine the practical time scale needed to execute meaningful critical fluid space experiments and characterize the location and dynamics of density or phase domains within the sample.

Research Task Description: The experiment time-line allows observation of large phase domain homogenization without and with stirring after thermostat installation in the Critical Point Facility (CPF), time evolution of heat and mass after a temperature step applied to one-phase equilibrium sample, phase evolution and configuration upon going two-phase from one-phase equilibrium, effects of stirring on a low-g two-phase configuration, two-phase to one-phase healing dynamics starting from a two-phase low-g configuration, and quantifying the mass and thermal homogenization time constant of a one-phase system under logarithmic temperature steps. Two Critical Fluid Thermal Equilibration (CFTE) test cells will be developed to be flown in the European Space Agency's CPF, which is manifested on IML-1 for December 1991 launch. During the full experiment, accelerometry data, time correlated with the video records, will identify the compressible fluid dynamics associated with Shuttle acceleration events and provide the investigators with intuition about gravity effects in a non-vibration isolated Shuttle environment.

Progress to Date: The CFTE flight hardware cells were shipped to ESTEC in December 1989. Two spare flight cells were delivered in March 1990. Both sets of cells have maintained flight quality to-date. Several tests of the cells have been performed in the CPF engineering model (EM) and flight model (FM) to verify CPF mission functionality and temperature calibration. The one year delay in launch to December 1991 has raised the need for more tests. Also, the delay has caused the mission to be shortened by two days and current work to shrink the science time-line is occurring. Delivery of flight hardware has since allowed time to do science analysis in preparation for the mission data. Ground based lab hardware has been set up to do interferometry in a CPF-like configuration. The calculation of equilibrium state interferograms for any temperature and any g-level has been accomplished to predict fringe patterns expected.

Publications

"Critical Phenomena in Microgravity Environments", *Bull. Am. Phys. Soc.* 34, 718 (1989).

4. BIOTECHNOLOGY

Protein Crystal Growth in a Microgravity Environment

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NAS8-36611 (NASA Contact: K. Johnson, MSFC)

November 1989 - October 1990

Objectives: The long range objective for this research task is to develop systematic and reliable techniques and hardware for growing protein crystals in space. Studies will be performed to evaluate the potential for enhanced protein crystal growth under microgravity conditions. Fundamental studies of protein crystal growth, both on the ground and in space will be performed in order to identify the major parameters that affect protein crystal growth. The fundamental studies will be used to define science requirements to be incorporated into advanced hardware that permit investigators to dynamically monitor and control the major parameters in protein crystal growth.

Research Task Description: This research program involves a multidisciplinary effort to produce protein crystals in space of sufficient quality and size to permit molecular structural characterization by x-ray crystallography, while simultaneously providing basic ground-based experimental and theoretical supporting research to develop a better understanding of protein crystal growth and to determine if gravity plays a limiting role in the growth process. Beginning with the Apollo program and extending into the Spacelab program, it has been demonstrated that the microgravity environment can provide stable growth conditions that can result in crystals with improved homogeneity and fewer defects. In this program, a variety of proteins will be crystallized on space shuttle flights over a three-year period. Optimum techniques for reliably growing protein crystals under microgravity conditions will be developed. Initially, emphasis will be placed on modified vapor diffusion techniques such as the "hanging drop method" that is widely used for ground-based studies in protein crystal growth. Long-range plans include development of new methods for growing protein crystals, based upon the experimental and theoretical studies performed as part of this research program. A major goal is to develop advanced hardware that will be available for use on the Space Station.

Progress to Date: Protein crystal growth hardware for use on the space shuttle was developed during the period between Challenger and STS-26. The hardware was constructed at Teledyne Brown Engineering Company, based upon the experience gained with four mid-deck flights in 1985 and 1986. The hardware includes a temperature control module, replaces a mid-deck locker, and contains three trays that permit 60 vapor diffusion experiments.

The hardware was flown in the mid-deck on shuttle flight STS-26 in September 1988. Three of the proteins included among the experiments on this flight produced crystals that were suitable for complete x-ray diffraction analysis. These three proteins are γ -interferon, porcine elastase, and isocitrate lyase. The proteins had been studied extensively in crystal growth experiments on earth prior to the microgravity experiments. Analyses of the space-grown crystals included collection of three-dimensional intensity data sets with electronic area detector systems. Comparisons of the microgravity-grown crystals with the best earth-grown crystals obtained in numerous experiments demonstrate that the microgravity grown crystals of these three proteins are larger, display more uniform morphologies, and crystals of these three proteins are larger, display more uniform morphologies, and yield diffraction data to significantly higher resolutions. Analyses of the three-dimensional data sets by relative-Wilson plots indicate that the space grown crystals are more highly ordered at the molecular level than their earth-grown counterparts.

The hardware was flown again on STS-29 in March 1989. Problems were encountered on this mission, resulting in showers of small crystals in nearly all of the experiments. Despite these experimental problems,

crystals of γ -interferon, which were suitable for x-ray diffraction analysis, were obtained. Although these γ -interferon crystals were no larger than those obtained previously on earth, they confirmed the finding from STS-26 that the microgravity-grown crystals diffract to higher resolution than earth-grown crystals, and display relative-Wilson plots that indicate enhanced molecular order.

During 1990, protein crystal growth experiments were performed using the vapor diffusion apparatus on space shuttle flights STS-32 and STS-31. The STS-32 mission was the first opportunity to attempt experiments at 4°C, along with experiments conducted at 22°C. During the mission, there was an interruption of power to the 4°C unit, which invalidated that set of experiments. The 22°C experiments resulted in excellent crystals of isocitrate lyase, confirming the results obtained for this protein on STS-26. The microgravity-grown crystals of this enzyme displayed prismatic morphologies, in contrast to the dendritic growth crystals obtained on earth, and produced X-ray diffraction data that is far superior to that of the datasets collected from earth-grown crystals. In confirmation of the results obtained for this protein on STS-26, relative Wilson plots indicate that the isocitrate crystals grown on STS-32 are more highly ordered at the molecular level than the best crystals obtained from this protein in earth-based experiments.

All of the STS-31 experiments were performed at 22°C. This mission produced excellent crystals of human serum albumin. X-ray analysis indicated that the microgravity-grown albumin crystals yielded data of significantly higher quality than that obtained from the best earth-grown crystals of this protein. The STS-31 mission also produced crystals of an antibody fragment and of the protein canavalin; X-ray analyses of these crystals indicated that they diffract to higher effective resolutions than crystals obtained on earth.

Along with the hardware development program, a number of basic studies in protein crystal growth have been completed. Particular emphasis has been placed on methods for detecting initial nucleation events, using laser light scattering and other optical techniques. As part of this project, investigators at The University of Alabama in Huntsville have determined the phase diagram for crystallization of lysozyme. Other work supported under this contract at Georgia Institute of Technology has led to the development of an automated system for dynamic control of vapor diffusion rates. These studies will be combined together to define hardware and techniques for dynamic control and monitoring of protein crystal growth parameters.

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Electrophoretic Separation of Cells and Particles From Rat Pituitary and Rat Spleen

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Dr. Andrea Mastro

NAG 8-807

December 1, 1989- November 30, 1990

Objectives: 1) To determine the effects of microgravity on the electrophoretic separation of rat pituitary growth hormone (GH) cell subpopulations; 2) to determine the effect of spaceflight on the ability of separated cells to synthesize and secrete biologically active GH; 3) to evaluate the capability of the FFEU (free flow electrophoresis unit) to separate GH particles containing unique 20K or 22K GH forms (or their polymers); 4) to determine if exposure of the GH cell to microgravity affects packaging of GH molecules within the secretory granule and 5) to determine effects of electrophoretically separated pituitary particles on immune cell function.

Research Task Description: Previous results from 3 spaceflight experiments (SL-3, COSMOS 1887 and COSMOS 2004) show that rat pituitary GH cell function is significantly reduced after exposure of the animal to μg for 7-14 days. Since the musculoskeletal and immune systems are GH targets, and since they are negatively affected by spaceflight, this issue warrants further study. We hypothesize that μg induced a change in the molecular packing density of GH within the secretory granule of certain GH cell subpopulations. We believe that the consequence of this change would be diminished hormone potency. By separating the biological particles in space, we not only test the various hypotheses, we also test the resolving capability of continuous flow electrophoresis techniques in μg .

Progress To Date: Cells. A number of electrophoresis buffers have been tested with regard to their effects on cell viability, recovery and clumping and a rank order of acceptability have been made. Particles. Results from a recently completed and published study (Hayes, et al.) show that GH containing secretion granules show anodal migration in the McDonnell Douglas CFE device at 27.2 V/cm: 30 min, 10.2 ml/fraction/h. GH variants (oligomers) showed greater anodal mobility than monomeric forms, a result which shows heterogeneity of GH packaging. This study provides the first results which document feasibility of separation of GH variants by CFE, a critical step to a successful spaceflight experiment.

Publication

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Protein Crystallization Experiments in Cryostat

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Professor Alexander McPherson

Objectives and Task Description: To evaluate the characteristics and quality of protein crystals grown by the liquid-liquid diffusion method in microgravity. Specifically the experiments will utilize the Cryostat device designed and produced by DFRL and manifested for flight aboard IML-1 later this year. Prior to flight the Cryostat device is to be thoroughly tested for its ability to induce protein crystal growth under earth laboratory conditions employing specifically those proteins and solutions that will be utilized in the actual flight experiment. These include the proteins canavalin from the Jack Bean, catalase from bovine liver, and a plant virus, satellite tobacco mosaic virus. Improvements in the Cryostat device will be sought and any problems with the hardware are to be identified and corrected.

Progress to Date: A series of crystallization experiments have been carried out at both 22°C and 4°C using the proteins canavalin and catalase as well as with the virus STMV. These were carried out using the conditions intended for the flight experiment with variation of parameters, such as pH and precipitant concentration, around the mean values with the objective of optimization.

We have satisfied ourselves that the Cryostat device performs satisfactorily for the crystallization of all three types of samples under earth laboratory conditions. Crystals have reproducibly been obtained under a broad set of conditions and the optimal solution conditions have been identified.

The crystals that have been grown to date are morphologically identical to those grown by other methods, such as dialysis and vapor diffusion, in earth laboratory conditions. The quality and average size, though we have not accurately quantitated it, appears to be the same as those produced by the other methods as well.

We are, for all practical purposes, now well prepared for the flight experiment and believe conditions have been optimized. We will, however, continue testing and reaffirmation of results and further assure ourselves that the device is fully flight worthy.

Publications

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Enhanced Hybridoma Production Using Electrofusion under Microgravity

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NAG8-716 (NASA Contact: S. Gonda, JSC)

October 1989 to October 1990

Objectives: Although newer, molecular techniques have now been introduced to prepare monoclonal antibodies, hybridoma technology remains critical to the production of monoclonal antibodies for use in a variety of biomedical applications. This technology relies upon immunological manipulation of lymphocytes, selection of suitable fusion partners, cell fusion and the selection of hybrids. All of these processes are, in turn, dependent upon a thorough understanding of cellular and subcellular processes underlying lymphocyte activation, regulation of the cell cycle, cell membrane biology and fusion. All of these processes are also central to many other biotechnological applications.

For the past year, we have conducted a series of studies directed at studying the biology of cell fusion and hybridoma production. The purpose of these studies has been to lay the groundwork for improvement of hybridoma technology, in general, and specifically, to provide a framework for the study of the effects of gravity on cell activation and cell fusion (which will be studied in a separately-funded flight proposal to be flown on the D-2 STS-mission).

These studies have been focused on the following specific aims:

- 1) Mechanisms of lymphocyte activation and propagation.
- 2) Mechanisms of immunological learning, antibody isotype switching and affinity maturation.
- 3) Development and optimization of methods for the purification and analysis of cellular membranes of lymphocytes during activation and cell fusion.
- 4) Evaluation and optimization of cell fusion experimental methods to obtain higher fusion yields and hybridoma recovery.

Research Task Description:

1) Mechanisms of lymphocyte activation and propagation

These studies have focused on both T-dependent and T-independent murine B cell activation. We have developed a model system of T cell-independent B cell activation that allows relatively long-term (14 day) propagation of certain murine B cell subpopulations, specifically B cells bearing relatively small amounts of the heat stable protein recognized by the monoclonal antibody, J11d (J11d^{lo} cells). These cells have been shown to be enriched for secondary B cell precursors. We have shown that the elimination of J11d^{hi} cells substantially increases the duration and extent of lipopolysaccharide/dextran sulfate mediated B cell proliferation. We are currently investigating the mechanism underlying this observation. We have observed that the J11d^{hi} B cell population is enriched for potentially regulatory CD5⁺ B cell population. One hypothesis that we are evaluating is that CD5⁺ cells produce "inhibitory immunoglobulins" that serve to dampen or suppress T-independent B cell proliferation. The elimination of this population might therefore result in enhancement of the T-independent proliferative response.

We have also used model systems for B cell activation developed principally for space flight. The preponderance of evidence to date would suggest that lymphocytes may be unresponsive to stimulation

in vitro by soluble activating agents, but may respond to cell-cell mediated activation. We have therefore developed a system based upon anti-T cell receptor monoclonal antibody activation and CD4⁺ T-B cell collaboration. We have found that this system efficiently activates and induces proliferation as well as differentiation of defined B cell subpopulations.

In addition to the initial cell-cell contact, a variety of regulatory substances may profoundly influence B cell responses. Various B cell subpopulations may differ substantially in their responses to such regulatory agents. To better understand factors influencing T-dependent B cell activation and to devise strategies for maximizing B cell activation, we examined the effect of cytokines on B cells activated using anti-CD3 bead stimulated CD4⁺ T cells (3). These studies showed that both interleukin 2 and interleukin 4 significantly increase immunoglobulin production by polyclonally activated B cells. In contrast, neurotransmitters such as Substance P, and Vasoactive Intestinal Peptide had either no effect on, or diminished immunoglobulin secretion (depending upon the source of the B cells used).

We are further evaluating the role of interleukins 5 and 6 and combinations of regulatory molecules in an attempt to optimize stimulatory conditions for B cell activation, proliferation and differentiation using both T-independent and T-dependent polyclonal activation models.

2) Mechanisms of immunological learning, antibody isotype switching and affinity maturation

One of the major goals of this project for the past year has been to establish conditions that maximize access to pure populations of fusible cells producing antibody with high affinity for preselected antigens. For this purpose, we have used the transfer of defined B and T cell subpopulations for the reconstitution of severe combined immunodeficiency (SCID) mice. This represents a preferred model system since, once conditions are maximized for murine cells, SCID mice, which themselves are devoid of an immune system, can also act as a vehicle for the stimulation of transferred human cells.

The production of high affinity antibody is dependent on the process of "immunologic learning" which accompanies the generation of "memory" B cells. "Immunologic learning" describes the increase in the quality (affinity) of antibody during the weeks following immunization. This is dependent on a dual process involving a) selective stimulation among the responding population of B cells with the highest affinity receptors for antigen, and b) the rapid accumulation of somatic mutations that change the specificity of responding cells, providing B cells with novel high affinity receptors. We have shown that the generation of memory B cells and somatic mutations in mice is relegated to a minority (10-13%) B cell subpopulation which can be enriched by virtue of its low expression of the cell surface antigen recognized by the J11D monoclonal antibody (J11D^{lo}). We have also shown that memory responses can be selectively regenerated in SCID mice by the transfer of J11D^{lo} precursor cells and T helper cells (T_H).

In order to fulfill the goals of this program we have assessed the generation of memory responses and immunologic learning in SCID mice reconstituted with J11D_{lo} precursor cells and TH under various conditions. Our results to date have confirmed that this protocol reproducibly enables the generation of large numbers ($2-8 \times 10^6$) memory B cells specific for the immunizing antigen 2,4-dinitrophenyl-hemocyanin (DNP-Hy). Memory B cells can be found as early as 4 days after transfer and primary stimulation, and for several months thereafter. We have tested several antigen doses and found that responses are maximized at relatively high doses (250 μ g).

We have now succeeded in measuring the affinity of numerous hybridoma antibodies obtained from SCID recipients secondarily immunized at various times after immunization. Our findings indicate that the average affinity of hybridoma antibodies generated by boosting 8 days after reconstitution and primary stimulation was 1×10^6 ; whereas, the average affinity of antibodies for mice boosted at 39 days, when substantial learning should have occurred, was 2×10^6 . Thus, relatively little immunologic learning was observed. Therefore, we are attempting to increase the ultimate affinity of recovered antibodies by several strategies. These include: a) the use of suboptimal amounts of immunizing antigen, b) the use of passive antibody to decrease effective *in vivo* antigen concentration, c) the use of higher numbers of transferred TH, and d) supplementation with other lymphoid cell subpopulations.

3) Development and optimization of methods for the purification and analysis of cellular membranes of lymphocytes during activation and cell fusion

Investigation of biomembrane structure associated with activation of T and B lymphocytes is essential for elucidation of the basic mechanisms responsible for normal functioning of the immune system. To facilitate biomembrane studies, improvements in basic separation and analysis technologies are required. During the past year we have concentrated our separation techniques on the use of free flow electrophoresis (FFE) to achieve our objectives. We have used the Hirschmann ACE 710 FFE instrument to document the usefulness of FFE as a research tool in monitoring biomembrane changes associated with electric pulse application (essential for electrofusion).

One difficulty encountered in these studies was the need for relatively large numbers of highly enriched cell populations from which membranes are prepared. This problem has been addressed by enriching for specific B cell subpopulations, activating and propagating them in sufficient numbers for membrane preparation using lipopolysaccharide and dextran sulfate (1). By flow cytometric analysis, we have shown that these cultures are greater than 90% enriched for J11d¹⁰ B cells.

The Hirschmann 710 FFE makes analytical separation feasible. However, preparative collection of biomembranes has remained elusive with this technology. During the past year, our program has partially supported the acquisition of novel patented technology developed at the University of Arizona. This technology permits separation of biomembranes with resolution comparable to that attainable with the Hirschmann apparatus, but is also capable of fractionation of preparative amounts of cell membranes as well as membranes of intracellular organelles. These studies have been done in collaboration with Dr. D. James Morré at Purdue University and with Dr. Ned B. Egen and Mr. Garland E. Twitty of the University of Arizona.

In addition, we have completed work on a computer-assisted program for image analysis of 2-D polyacrylamide gel patterns. These programs are important for the elucidation of the gene product changes associated B lymphocyte activation. Taken together, these studies have and will continue to allow us to advance our understanding of basic mechanisms and changes associated with the transition from the nonactivated to the activated state and the relationship of structure and function.

4) Evaluation and optimization of cell fusion experimental methods to obtain higher fusion yields and hybridoma recovery

The T cell independent B cell activation system (1) for production of enriched populations of activated B cells has led to a reproducible source of fusible cells needed to optimize the electrofusion conditions. In order to obtain greater yields of hybridomas we have tested different combinations of electrofusion conditions and buffers. In addition, we have begun a mathematical analysis of the forces engaged during alignment of cells during electrofusion. As a result it is now routinely possible to obtain yields of one hybridoma per 500-1,000 activated B lymphocytes.

Our ultimate objective is to obtain sub-populations of B cells specific to given antigens (see objective 2). These efforts have used T cell mediated activation approaches and were developed in parallel and funded independently through our NASA flight contract.

Because some B cell sub-populations represent a very small proportion of cells, a need for an instrument capable of fusing as few as 10,000 B cells was developed. This device is capable of yielding as many as 1,000 hybrid clones from a starting number of 10,000 fusible B cells. Future studies will focus on the use of our newly acquired FFE methods, magnetic force separation methods, and flow cytometry methods to select for limited numbers of selected subpopulations of B cells.

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5. GLASSES AND CERAMICS

Measurement of Liquid-Liquid Interfacial Tension and the Role of Gravity in Phase Separation Kinetics of Fluid Glass Melts

University of Arizona
Dr. Michael C. Weinberg
Dr. George F. Neilson

Objectives: The objectives of this flight program are: (1) to measure the liquid-liquid interfacial tension, as a function of composition, for a phase separating glass system, and (2) to measure the phase separation kinetics of a glass which tends to micro-segregate on earth.

Research Task Description: Liquid-liquids interfacial surface tensions have not been measured by direct means for any immiscible glass systems. Since, however, the surface tension is one of the key parameters which enters into theories of phase separation kinetics, it is important to find procedures by which this quantity can be measured. The liquid-liquid surface tension between end member compositions of a phase separating PbO-B₂O₃ glass will be measured in a containerless facility in microgravity. The measurement will be made by recording the distortion of a compound drop (consisting of the two end member compositions) which is subjected to rotation. The ratio of minor and major axes of the inner drop, when the compound drop is rotating at constant angular velocity, allows for the determination of the surface tension between the two liquids.

Progress to Date: Since a high temperature levitation facility which could accommodate our experiment was unavailable for USML-1 and we considered it prudent to demonstrate the feasibility of our approach on a simpler system, we decided to select systems consisting of immiscible organic liquid pairs which can be studied at room temperature. During the past nine (9) months several candidate systems have been identified and their important physical parameters have been tabulated. In addition, theoretical calculations have been performed in order to determine the requirements on the initial radius ratio of inner to outer drop which must be imposed. These constraints arise from the desire to avoid bifurcation of the outer drop and to prevent the inner drop from penetrating the surface of the outer drop. Also, calculations have been performed in order to determine the rotation rates which should be employed in the experiment.

Publications

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6. COMBUSTION SCIENCE

Scientific Support for an Orbiter Middeck Experiment on Solid Surface Combustion

Mississippi State University
Professor Robert A. Altenkirch
Dr. S. Bhattacharjee
Mr. Jeff West
NAS3-23901 (NASA Contact: Kurt Sacksteder, LeRC)
December 19, 1984-December 20, 1992

Objectives: The overall objectives of the experiment are to: (1) determine the mechanism of gas-phase flame spread over solid fuel surfaces in the absence of any buoyancy induced or externally imposed gas-phase flow; and (2) improve the fire safety aspects of space travel.

Research Task Description: The spread of flame in the gas over the surface of a solid combustible involves in an essential way the transfer of heat from the flame to the solid fuel immediately ahead of it. This heat transfer is affected by the character of the gas-phase flow, and so the phenomenon of flame spreading under reduced gravity, in which the flow is generated by the gasification of the solid combustible and movement of the flame, is apt to be different from what occurs under the Earth's normal gravitational acceleration where the flow is largely buoyancy driven.

An experiment has been designed for the Middeck of the Space Shuttle to aid in understanding the process of flame spreading in the absence of a buoyancy-driven flow. A chamber of approximately 0.035 m^3 in volume is to contain either a thin sample of a cellulosic material or a thick sample of polymethylmethacrylate and an oxidizing environment of O_2 and N_2 . Samples will be ignited at one end, and the ensuing flame spread process will be filmed. The spread rate can be determined from the films, and surface and gas-phase temperatures just above the surface will also be recorded. A matrix of eight experiments to be carried out on the Middeck has been identified. These data will help to clarify the mechanism of forward heat transfer in the low-gravity flames.

The experimental apparatus has been constructed at NASA's Lewis Research Center and tested in the Drop Tower facilities. Methods of data reduction and theoretical analyses of the reduced-gravity flame spread problem have been developed and are being refined. Results to date show that measured spread rates over thin cellulosic fuels are less at microgravity than for downward spread in normal gravity. Theoretically predicted spread rates not accounting for any effects of radiation heat transfer are generally higher than what is measured. Inclusion of surface reradiation in the modelling reduces the predicted spread rates and brings them more in line with experiment. Gas-phase radiation provides a feedback mechanism to the solid and a loss mechanism to the environment such that the effect of gas-phase radiation on the flame spread rate is rather complicated. Consideration of gas-phase radiation results in predicted spread rate trends that qualitatively compare favorably with experiment.

Progress To Date: Computational methods for determining gas-to-solid heat flux from experimental solid-surface temperature data for thin solid combustibles have been developed and applied to experimental drop tower results. The steady-state, computational model is now able to account for finite-rate gas-phase and solid-phase chemistry, surface reradiation, and gas-phase radiation. Both thermally thin and thermally thick fuels can be considered, and work on unsteady analyses to track the flame spread event from ignition to steady state or extinction is underway.

The first matrix point of the SSCE experiment was flown on the Discovery mission launched October 6, 1990. Indications are that the experiment performed as designed without flaw. Results from the experiment are now being examined, interpreted, and compared to theory.

Publications

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C. PHYSICS AND CHEMISTRY EXPERIMENTS (PACE)

Precise Viscosity Measurements Very Close to Critical Points

National Institute of Standards and Technology

Dr. Robert F. Berg

Dr. Michael R. Moldover

C-32001-K (NASA contact: Dr. R. Allen Wilkinson, LeRC)

October 1, 1989 - November 30, 1990

Objectives: Our objective is to accurately measure, in microgravity, the viscosity of xenon near its liquid-vapor point critical point. The space experiment will be the fourth in a series of studies of dynamic critical phenomena. These are: (1) theoretical studies, (2) viscosity measurements of binary liquid mixtures, (3) viscosity measurements of pure fluids in 1-g, and (4) viscosity measurements of xenon in low gravity.

Research Task Description: Near the critical temperature T_c the viscosity η is predicted to diverge as:

$$\eta \sim (T - T_c)^{-\gamma}.$$

Prior to this work, this functional form had been verified for binary mixtures near their consolute points but with apparent exponents γ ranging from the theoretical value (0.032) to as high as 0.042. In pure fluids near their liquid-vapor critical points, experimental values of γ were even more uncertain, in part because of gravitational stratification near T_c . The scientific task is to improve the measurement of γ , first on earth and then in a microgravity environment.

Progress to Date: We have developed a unique series of torsion oscillator viscometers devoted to critical point measurements with both low frequency and low shear operation in a thermostat with sub-millikelvin thermal perturbations. Their application to four binary mixtures narrowed the experimental range of the exponent to $0.040 < \gamma < 0.044$, a result inconsistent with theory. We have also measured the viscosity of CO_2 and xenon near their critical points. The xenon measurements will be an essential input for analyzing the results of the Zeno microgravity light scattering experiment. Analysis of the carbon dioxide and xenon data, which incorporated both modern crossover theory and 1-g stratification effects, gave exponents in the range $0.040 < \gamma < 0.042$. The consistency of our results for the binary mixtures and pure fluids is the most convincing evidence that both types of fluids are in the same dynamic universality class.

Measuring the viscosity in low gravity will allow the exponent γ to be determined without relying on the uncertain details of the theory for crossover from the noncritical to the critical region. However, the inherent vibration sensitivity of the existing 1-g viscometer requires an acceleration environment of less than $4 \times 10^{-8} \text{ g/Hz}^{1/2}$ near the viscometer's resonance at 1 Hz. This is a serious engineering challenge. In order to reduce the severity of this vibration specification, we are investigating the feasibility of manufacturing a miniature viscometer consisting of a transducer moving inside the sample container. Theoretically, miniaturization reduces the sensitivity to vibration. (In the present torsion oscillator scheme, the sample container itself is the moving element.)

Related work includes the measurement of the viscosity of a polymer solution near its critical consolute point and the fabrication of a low-power mixer suitable for fluids near critical points. As collaborators in the Thermal Equilibration Experiment, we also have assisted in the fabrication and loading of sample cells and in the determination of the critical temperatures of the flight samples in the flight model of the Critical Point Facility, scheduled for the IML-1 Shuttle Flight.

Publications

R.F. Berg and M.R. Moldover, "Critical exponent for the viscosity of carbon dioxide and xenon", J. Chem. Phys. 93, 1926 (1990).

Bubble-In-Liquid Mass Transport Phenomena in a Reduced Gravity Environment

University of Toledo
Professor Kenneth J. De Witt
Chain-Nan Yung
Jonathan L. Brockwell, Union Carbide Technical Center
NAG3-334 (NASA Contact: A.T. Chai, LeRC)
October 1989 - October 1990

Objectives: The objective of the experiment is to determine the merits/feasibility of a space experiment to study mass transport phenomena and interfacial dynamics of a gas bubble dissolving in a liquid. Multiple bubbles and movement due to thermocapillary or diffusocapillary migration are also considered. A numerical model has been developed which simulates the bubble dynamics under reduced gravity conditions and can be used to analyze bubble behavior and to determine transport parameters by comparison with the experimental data. The results will yield information that will have application to many problems in physical chemistry and technology.

Research Task Description: The approach consists of experiments and numerical modeling. The modeling of the dissolution of a single bubble or of a moving bubble due to residual gravity effects has been accomplished. Present modeling involves incorporation of thermal and concentration gradients at the interface. Ground-based and drop-tower experiments include bubble and droplet motion due to an interfacial tension gradient and electrical effects. The justification for conducting the experiment in space is the elimination of large-scale buoyant bubble motion and free convective mass transfer effects that occur in normal gravity. These effects generally mask the molecular mass transfer and interfacial contributions to the dissolution process, and their elimination would allow a more fundamental understanding of the molecular mass transfer and interfacial efforts to be obtained.

Progress to Date: The Preliminary Science Requirements Document was finished along with the Engineering Design Document. The Conceptual Design Review was held in January 1990, and the Science Panel suggested broadening the scope of the experiment. The scope of the experiment has been enlarged to include multiple bubbles and their interactions, along with movement due to thermal, concentration, and electrical effects.

Publications

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Determination of the Correlation Length in Helium II in a Microgravity Environment

University of Oregon

Dr. Russell J. Donnelly (P.I.)

Dr. Joseph J. Niemela

(NASA Contact: Dr. Donald Strayer, J.P.L.)

Objectives: The objective of this research is to measure finite size effects in the isobaric expansion coefficient, α_p , near the lambda transition, T_λ in liquid helium. Finite size effects are manifested as a rounding of the divergence in thermodynamic functions near a critical point as the correlation length increases toward the system size. We can thus test renormalization group theory predictions, universality assumptions, and boundary conditions.

We will measure α_p for liquid helium confined between parallel plates for a range of temperatures very near T_λ (both above and below), a range of pressures from SVP to about 25 bar, and a range of plate separation distances. In order to measure finite size effects very near T_λ or with a very well-characterized macroscopic geometry, we need a plate separation which would result in an extremely inhomogeneous sample in the earth's gravitational field; a microgravity environment eliminates this problem.

Research Task Description: We will measure the dielectric constant of helium confined between parallel plates as a function of temperature at constant pressure. Using the Clausius-Mossotti relation, we can calculate the density and thus the expansion coefficient of liquid helium. The experimental method involves two measurements, at a given temperature, of the balancing ratio of an audio-frequency ratio-transformer capacitance bridge, one with the sample capacitor empty and then filled with helium. Appropriate division of these ratios then yields directly the dielectric constant at that temperature.

The capacitor used to measure the dielectric constant is a parallel plate design operated as a three-terminal device in a 1 kHz ratio-transformer bridge. The spacing between the electrodes is determined by a precision shim which can be easily changed. An identical capacitor is also mounted on the experimental platform and is operated empty as a reference capacitor. We expect to vary the thickness of the shims between 5 μm and 5 μm .

High resolution temperature measurements will be made using a paramagnetic salt thermometer identical to that used by John Lipa in his lambda-point heat capacity experiment, currently scheduled for flight in 1992.

Progress to Date: A new apparatus probe is nearly completed in the University of Oregon machine shop. This new probe is versatile and will allow several different experiments to be run simultaneously. John Lipa's group at Stanford is providing assistance on the design and operation of the high resolution thermometer. This new thermometer should be much less susceptible to vibrational noise than the previous cavity thermometer. The new capacitors represent a considerable improvement over the previous niobium cavities in the sense that they are easily serviceable (the old ones were not serviceable at all) and they will allow us to vary the gap size with no additional machining of the apparatus. Additional improvements include the use of extra isolation stages and a radiation shield surrounding the experiment at nominally the same temperature. The ratio transformer bridge should be relatively straight-forward to use and we expect the experiment to progress smoothly, starting with the initial low-resolution measurements of dielectric constant in Spring, 1991.

Satellite Test of the Equivalence Principle (STEP)

W. W. Hansen Experimental Physics Laboratory, Stanford University
Professor C. W. Francis Everitt
Dr. Paul W. Worden, Jr.

Objectives: The objective of this research is to test the equivalence of inertial and passive gravitational mass in an Earth-orbiting satellite. We have done preliminary work and technology development with a ground-based version of the apparatus that could test equivalence to about one part in 10^{12} . Recent studies show that the satellite version of this experiment should have a sensitivity better than one part in 10^{17} of the total rate of fall. We envision the satellite experiment being performed as a joint NASA-ESA collaborative mission.

Research Task Description: The requirements for an orbital experiment have been well defined by studies using the Earth-based apparatus. The experiment consists in comparing the motions of concentric cylindrical test masses suspended in precision superconducting magnetic bearings and free to move along their common axis. The materials are chosen according to the best theoretical likelihood of an effect, and the masses, weighing about 1 kg each, are plated with superconductor to make them uniformly controllable. A position detector based on SQUID magnetometers measures both differential and common mode motion of the test masses. This makes an accelerometer sensitive to 10^{-14} cm/sec² or less. The remainder of the apparatus controls the positions of the test masses and isolates them from disturbances. Essential features include a drag-free spacecraft with acceleration levels of about 10^{-11} g/ $\sqrt{\text{Hz}}$; a mass positioning servo which uses the acceleration from the Earth's gravity gradient to center the masses on each other within 0.2 Å, a charge measurement and control system to limit the effects of cosmic ray charging; a method of controlling liquid helium sloshing; and superconducting shields for electromagnetic isolation.

We expect to be able to compare six test masses in a single six-month mission. The spacecraft would be an 800 kg free orbiter in a 550 to 750 km high, Sun-synchronous orbit. A version of this experiment performed on Shuttle would be severely limited by vibrations and drag; extreme care, together with some modification to the Shuttle attitude control system, could reach no better than 10^{-14} . The free orbiter should reach 10^{-17} and will be limited mostly by gas pressure effects and residual acceleration in the drag-free system.

Progress to date: In November 1989, STEP was selected as a potential candidate for the European Space Agency's Next Medium-Sized (M2) Mission. Dr. Worden spent most of the summer and fall of 1990 participating in a feasibility study of STEP at the European Space Technology Engineering Center (ESTEC), Noordwijk, Holland, and he and Professor Everitt have formed the basis of a NASA-ESA collaboration on STEP by identifying and visiting interested groups in France, Germany, Italy, Switzerland and England. The ESTEC Study concluded that STEP is feasible. In June 1991, ESA will select four of the six candidate missions for a Phase A Study.

The proposed experiment layout is based on interfacing the instrument with existing Lockheed small flight dewar. The instrument package was designed by Mr. Matthew Bye, who this year has been appointed Manager for STEP Hardware Development. We gratefully acknowledge the financial support to the program provided this year by the Stanford Dean of Research, and by the PEW Science Program which funded a summer fellowship for an undergraduate student Mr. Wipul Jayasekara.

Publications

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Worden, P. W., Everitt, C. W. F., Bye, M., Satellite Test of the Equivalence Principle Science Requirements Document, (May 1990).

Critical Fluid Light Scattering (Zeno)

University of Maryland
Professor R. W. Gammon
Dr. J. N. Shaumeyer
NAG3-849, NAS3-25370 (NASA Contact: R. Lauver, LeRC)

Objectives: The objective is to measure the decay rates of critical density fluctuations in a simple fluid (xenon) very near its liquid-vapor critical point using laser light scattering and photon correlation spectroscopy. Such experiments are severely limited on earth by the presence of gravity which causes large density gradients in the sample. The goal is to measure fluctuation decay rates with 1% precision two decades closer to the critical point than is possible on earth, with a temperature resolution of ± 3 microKelvin. This will require loading the sample to 0.1% of the critical density and taking data as close as 100 microKelvin to the critical temperature ($T_c = 289.72$ K). The minimum mission time of 100 hours will allow a complete range of temperature points to be covered, limited by the thermal response of the sample. Other technical problems have been addressed such as multiple scattering and the effect of wetting layers.

Research Task Description: We have demonstrated the ability to avoid multiple scattering by using a thin sample (100 microns), and a temperature history which can avoid wetting layers, a fast optical thermostat with satisfactory microcomputer temperature control and measurement, and accurate sample loading. There remain the important engineering tasks of mounting the experiment to maintain alignment during flight and using vibration isolation to prevent Shuttle motions from distorting the sample.

The experiment entails measurement of the scattering intensity fluctuation decay rate at two angles for each temperature and simultaneously recording the scattering intensities and sample turbidity (from the transmission). The analyzed intensity and turbidity data gives the correlation length at each temperature and locates the critical temperature.

The fluctuation decay rate data set from these measurements will provide a severe test of the generalized hydrodynamics theories of transport coefficients in the critical region. When compared to equivalent data from binary liquid critical mixtures they will test the universality of critical dynamics.

Progress to Date: The design evolved and was presented at the Preliminary Design Review in October. The design features now two photomultipliers and a correlator card capable of processing two autocorrelation functions so that forward and backward scattering measurements can be done simultaneously. A new active vibration isolation system is included.

Following the suggestion of A. Onuki that temperature changes were greatly speeded up by adiabatic effects has lead to three manuscripts were published in February 1990, one each by the Zeno group, by Onuki, Hao and Ferrell, and by Zappoli, Bailly, Garrabos, Le Neindre, Guenoun and Beysens all showing some version of this effect in calculations. The startling conclusion is that near the critical-point temperature changes can occur to within 1% of their final value in seconds and this gets faster the closer the sample is to the critical point. A first video demonstration of this effect was made and a manuscript with a quantitative measurement of the fast temperature changes was accepted for publication in Physical Review Letters.

A design audit was completed in June with a bout 75% of the drawings finished for the Engineering Development Model (EDM) of the Zeno instrument. Essentially all of the hardware for the EDM is complete and the system integration began in September. The Critical Design Review is planned for March 1991.

Publications

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J.N. Shaumeyer, R.W. Gammon, and J.V. Sengers, "Measurement of Diffusivities with Photon-Correlation Spectroscopy," IUPAC Volume on Measurement of Transport Properties, in press.

Presentations

Gammon, R. W., "The Zeno Experiment: Microgravity Critical Fluid Light Scattering in Earth Orbit," University of Maryland, Physics Department Colloquium, October 23, 1990.

Heat Capacity Measurements near the Lambda Point of Helium

Stanford University
Professor John A. Lipa
Dr. T.C.P. Chui
Dr. D. R. Swanson
Dr. J. Nissan
Dr. U. Israelsson, JPL
JPL 957448 (NASA Contact: R. Ruiz, JPL)
January 1, 1990 - December 31, 1990

Objective: Central to condensed matter physics is the phenomenon of second order phase transitions. These come about when a wide class of interactive terms are added to the simple ideal gas picture of matter. To understand condensed matter in general, it is necessary to address the phase transition issue, since these are involved in nearly all the interesting effects observed. Our goal is to perform the most stringent test currently feasible of the present theory of second order transitions in the asymptotic limit as the transition is approached. To do this we will measure the heat capacity of helium very close to its lambda transition at 2.1K.

Research Task Description: To perform the heat capacity measurements, two main requirements must be met: first we must have sufficient temperature resolution to establish the temperature scale, and second we need to control the energy input to the sample to determine its heat capacity. To these ends we have been developing a new high resolution thermometer and an advanced, multi-layer thermal control system. The thermometer makes use of superconducting technology to achieve a resolution of about 3×10^{-10} deg in a 1 Hz bandwidth, and the thermal control system can achieve a power resolution approaching 10^{-12} W. These two systems give us the capability to make measurements to the limits imposed by the Shuttle environment. A third requirement is to achieve an operating temperature of 2.1 K. To do this we make use of the superfluid helium research facility previously flown on Spacelab-2 by JPL.

Progress to Date: By early '90 the instrument electronics had been procured from Ball Aerospace and the cryogenic probe had been fabricated. Instrument testing occurred between January and August when the apparatus was judged ready for integration with the flight dewar at JPL. Both the thermometry and the thermal control system were found to operate as expected. After shipment to JPL some portions of the electronics were subjected to a thermal/vacuum test and the instrument was installed in the dewar. The testing of the interface between the instrument electronics and the dewar electronics was also successfully completed. Some delays were encountered due to low temperature leaks in the dewar, but by the end of the year we were ready to commence integrated systems testing. We expect to ship to KSC in November 1991 in preparation for a late 1992 launch as part of the USMP-1 payload.

Publications

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T.C.P. Chui and D.R. Swanson, "The Effects of Gravity in Second Sound," in *Proceedings of Low Temperature Physics Conference*, LT-19, Aug. 1990.

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Critical Transport Phenomena in Fluid Helium Under Low Gravity

Duke University

Dr. Horst Meyer

NAG 5-379 (NASA Contact: Stephen Castles, GSFC)

January 1, 1990 - December 31, 1991

Objectives: These are to measure the shear viscosity η in ^3He - ^4He mixtures near the tricritical point ($T_t = 0.87\text{ K}$, $X_t = 0.67$) where X and T are the ^3He concentration and the temperature, respectively. One could expect, by analogy with the behavior near the liquid vapor critical point, that η near (T_t, X_t) would also weakly diverge. In this case, the earth's gravity will produce a rounding of this divergence, because of the induced density gradients in the fluid layer. In the absence of gravity, this rounding should then disappear.

The first question to resolve is whether or not η near the tricritical point of helium mixtures really diverge. There is no formal theory making a prediction, although measurements on a ternary mixture at room temperature near its tricritical point shows a divergence. For this purpose we have started a systematic study of the viscosity of ^3He - ^4He mixtures with particular emphasis on their superfluid transition curve $T_\lambda(X)$ which terminates at the tricritical point.

Research Task Description: The viscosity is measured by means of a torsional oscillator operating in a continuous mode at the frequency of 150 Hz, as described in our recent publication. The horizontal fluid layer in our present cell is $\sim 0.04\text{ cm}$ high with a diameter of 5 cm and is contained in a thin walled beryllium-copper cell that oscillates around its axis with an extremely small amplitude detected electronically. The apparatus measures the product $(\rho\eta)$ where, in the *normal* phase of the mixture, ρ is the mass density determined in a small cell situated above the torsion oscillator. In the *superfluid* phase ρ is the density of the normal component and is determined from separate experiments as described in our publication. Combination of the two measurements then finally gives the viscosity η .

Progress to Date: We have started operating a new cryostat enabling us to extend the temperature range down to temperatures of 0.5 K to permit the investigation of the tricritical point. After an exhaustive test with dilute mixtures of ^3He in ^4He , we have conducted measurements of $(\rho\eta)$ for a number of mixtures near the tricritical point. Several standard mixtures were prepared, and once the measurements with each were completed, the concentration of the fluid was changed by small steps by means of removing a small fraction and adding a known amount of either ^3He in ^4He . In this way we systematically investigated $(\rho\eta)$ for $X = 0.50$, $0.58 \leq X \leq 0.74$, 0.80 and 1.00 and we are in the process of diluting the mixture $X = 0.58$, presently under investigation. These are time-consuming experiments, because of the long equilibration times in the superfluid phase. We have developed and gradually improved the software for automatic data acquisition and analysis of the simultaneous $\rho\eta$ and ρ measurements.

A presentation of the results has been made at the 1990 spring meeting of the American Physical Society in Washington. The most up-to-date presentation was the Low Temperature Workshop organized by the University of Oregon at Washington, DC in January 1991.

The principal result is that there is a singular behavior of η along the line of superfluid transition $T_\lambda(X)$, resulting in a peak that emerges for $X > 0.50$. However, as the tricritical point is approached, this peak merges with the temperature-dependent background viscosity, and as $X \approx X_t$, it can no longer be clearly seen. As a result, it appears doubtful that η has a weak divergence at T_t , in contrast to the behavior near the liquid-vapor critical point.

Publications

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H. Meyer, C. Howald, X. Qin and H.S. Nham, "Shear Viscosity of ^3He - ^4He Mixtures Near the Tricritical Point," in *Proceedings of Low Temperature Physics Workshop, Eighth University of Oregon Conference on Low Temperature Physics*, Washington, DC, January 1991.

Studies in Electrohydrodynamics

Princeton University

Dr. D. A. Saville

NAG 3-259 (NASA Contact: Dr. R. Balasubramanian, LeRC)

Objectives: The purpose of this work is to develop and test models of electrohydrodynamic processes involving fluid interfaces. Particular attention is given to the behavior of fluid globules in systems with poorly ionized solutes at high (applied) field strengths. An ad hoc model (the leaky dielectric) described by G. I. Taylor and J. R. Melcher will be expanded so as to include electrokinetic effects and put it on a firm theoretical basis.

Research Task Description: Extant theories which account for the details of physico-chemical processes associated with charged interfaces deal exclusively with low field strengths and fully ionized solutes. The model now used to describe processes at high field strengths -- the leaky dielectric -- omits consideration of electric double-layers, adsorption at interfaces, and chemical processes involved in the dissociation and recombination of solute species. Thus, even though the model depicts some features associated with bulk fluid motion faithfully, it fails to give a comprehensive picture.

The research involves several tasks: (i) construction of a mathematical model describing low field strength electrokinetics with fluid globules wherein the interface is permeable to ions and the electrolyte contains poorly ionized solutes, (ii) extension of the model described in (i) to high field strengths, (iii) adaptation of the model to oscillating fields and (iv) experiments involving steady or oscillating fields with fluid globules to test the theory. The experiments will take advantage of a micro-gravity environment to overcome problems associated with sedimentation and buoyancy driven convection arising from Joule heating.

Progress to Date: The sample cell and high voltage electronics have been used to study the behavior of freely suspended droplets in strong electric fields. However, only a limited number of fluid pairs have been studied due to problems with droplet sedimentation - the host fluid must be very viscous. Castor oil and viscous silicon oils have been used as host fluids with castor oil, silicon oil and water droplets. Careful measurements of interfacial tension, fluid conductivities, and dielectric constants were made, along with drop deformation. Situations with both prolate and oblate deformations were studied in AC and DC fields. The agreement between theory and experiment is, thus far, excellent. The next task is to develop a technique to control the conductivity of the fluids using an ionic surfactant so as to be able to study a wider range of properties.

Publications

J. C. Baygents and D.A. Saville, "Electrophoresis of drops and bubbles," J. Chem. Soc. Faraday Trans., in press.

J. C. Baygents and D.A. Saville, "Electrophoresis of drops and bubbles in weak electrolytes," J. Colloid Interface Sci., in press.

Mechanics of Granular Materials

University of Colorado at Boulder,
Professor Stein Sture
NASW-2110

Objectives: The objective of the investigation of constitutive properties of cohesionless granular materials at various initial densities at very low confining pressures during proportional and non-proportional loading and associated material instability phenomena.

Research Task Description: In this period we are performing ground-based experiments on cylindrical specimens and focus on material bifurcation as well as continuum constitutive behavior. We are also conducting numerical simulation of specimen behavior at various confining stresses and levels of shear deformation. We are also assisting Sandia National Laboratories and Marshall Space Flight Center with experimental apparatus design and development.

Progress to Date: The effort started in June 1990 and we are making good progress in all areas, and we hope that both MSFC and SNL will become involved with the management of the project and apparatus design and development to a greater extent this year.

Publications

Peric, D., "Localized Deformation and Failure Analysis of Pressure Sensitive Granular Materials," Ph.D., University of Colorado, 1990.

D. FACILITIES

Microgravity Materials Science Laboratory

NASA Lewis Research Center
Thomas K. Glasgow
In-House

This laboratory was established to provide to researchers from industry, academia and government access to specialized equipment and experienced personnel to aid in development of space flight concepts, experiments, and hardware. The laboratory is equipped with a number of unusual experimental and computational facilities and staffed by engineers from several disciplines and technicians familiar with microgravity practice.

In the Microgravity Materials Science Laboratory (MMSL) investigators are encouraged to take the first steps toward defining space flight experiments for later performance on the space shuttle or on the space station. The laboratory may also be used in preparation for experiments to be conducted in other ground based, reduced gravity environments such as those provided by drop tubes, aircraft, or rockets. The computational facilities may be used to model the expected fluid flow and heat transfer in microgravity experiments. Another use of the Laboratory is for post flight investigations. The most notable example of this type of analysis was the post flight exposition of the convective effects in 3M's DMOS experiment. Work on DMOS and follow on modelling was essentially completed in 1988. One interesting finding was that even completely reversed accelerations can cause convective mixing and that even low accelerations, e.g. $10^{-6}g$, can cause bulk flow.

Among other equipment, the MMSL has a vacuum chamber large enough to accommodate a GAS can. This chamber will be used to perform ground based studies on thermal energy storage in phase change materials. There are also plans by Ohio State University and Rockwell to use the chamber for tests of a vacuum welding technique.

In conjunction with Westinghouse Corporation, the salt solidification furnaces of the MMSL were used to grow crystals of lead chloride and lead bromide. Both are opto-electronic materials potentially important for upcoming generations of computers and communication devices. Another industrial interaction was with Brimrose Corporation, manufactures of laser guidance equipment. Brimrose was awarded a phase one SBIR contract to study means of observing convection in crystal growth. They concentrated on high resolution thermography.

Other organizations working with the MMSL include GTE, Rockwell, Rensselaer Polytechnic Institute, Case Western Reserve University, Michigan Technological University, University of Akron, Cleveland State University, University of Kentucky, and Ohio State University. Discussions have been conducted with researchers from the Naval Surface Weapons Center concerning microgravity crystallization of high temperature semiconductors.

The MMSL facilities have been used by Francis Chairamonte of the Lewis Space Experiments Division for precursor work pertaining to his Learjet solidification project. He is investigating the formation of voids during solidification in microgravity; his real interest is in the influence of voids on heat transfer in practical space systems such as heat storage devices. His experiment has now flown on the learjet.

Telescience has been under investigation in a joint project with RPI. The major effort in this area has been devoted to the creation and testing of software required to link process controllers and video cameras to computers. A glass melting furnace has been remotely controlled. More recently, Dr. Johnston has demonstrated focusing of a microscope remotely (from Albany).

The MMSL has had a very active involvement in two ATD projects, Laser Light Scattering Instrument and High Temperature Furnaces. The Laser Light Scattering project has generated considerable interest for advancing to flight experiments, brought together many of the world's most active developers of this technology. There was general agreement that the most important pieces of hardware required for a compact, efficient, space flight version of the instrument will be available for testing the ATD project scientist, Bill Meyer, has been coordinating the specification of new compact lasers, new optical systems, special optical fibers, efficient, fast, solid state photon counters, and compact dedicated correlator computers.

High Temperature Furnace technology has been under development in-house and on grant. The in-house effort has concentrated on a modular approach to building efficient furnaces, including transparent furnaces, and on devising means of garnering real data for inclusion into furnace design and control models. A related effort has been the development of multizone control software necessary for flexible control of complex thermal profiles. On grant we have been investigating the feasibility of actively controlling advancing solidification interface position and shape by the use of directed energy sources; this work has resulted in a masters thesis.

While the original MMSL concept was to provide access to ground based functional duplicates of space flight hardware we have found the greatest use of lab provided facilities has been in the area of computational modelling. Therefore we have used a significant portion of our total funding to provide the equipment, software, and support staff in this area. In the past year the MMSL has co-sponsored an extensive study by Emily Nelson of the anticipated effects of the complex acceleration environment of the Space Station on materials science experiments. Publication of the study is planned for early CY91.

The Microgravity Materials Science Laboratory in addition to its computational facilities has equipment for observation of salt solidification and physical vapor transport, for planar front and dendritic growth from the liquid, for studying convection in mixing of liquids of slight density differences, for glass melting and solidification, for hot stage microscopy, for bulk undercooling, for levitation of conductive melts, and for solidification isothermally and in a gradient. Several presentations of MMSL capabilities are given each year at different symposia to inform the community of its availability. The laboratory also serves an educational role not only for the summer students typically employed but also for touring teachers and students, many receiving their first introduction to microgravity concepts.

Publications

Pines, V. K., and Taylor, P. L., "Stability and Instability in Crystal Growth: III. Reduction of the Thermodiffusion Equation for a Paraboloidal Needle Crystal," Phys. Rev. A, **41**, 1006, (1990).

Pines, V. K., Taylor, P. L., and Zlatkowski, M. A., "Stability and Instability in Crystal Growth: IV. Time Development of a Perturbed Paraboloidal Needle Crystal," Phys. Rev. A **41**, 1021, (1990).

Pines, V. K., Zlatkowski, M. A., and Chait, A., "Undercooling Experiments and the Wall Proximity Problem: Analytical and Numerical Study," *International Heat Transfer Conference*, Jerusalem, Israel, June 1990.

Pines, V. K., Zlatkowski, M. A., and Chait, "Time Development of a Perturbed Spherical Nucleus in a Pure Supercooled Liquid: I. Power Law Growth of Morphological Instabilities on Liquid-Solid Interface," Phys. Rev. A **42**, 6129-6136 (1990).

Pines, V. K., Zlatkowski, M. A., and Chait, A., "Time Development of a Perturbed Spherical Nucleus in a Pure Supercooled Liquid: II. Nonlinear Development of Morphological Instabilities and Formation of Predendritic Structure," Phys. Rev. A. 42, 6137-6150 (1990).

Ground Based Facilities

NASA Lewis Research Center
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In-House

A very high level of utilization continued to be experienced by the LeRC reduced gravity facilities in 1990. This is indicated by the level of testing in the facilities which are summarized as follows: 2.2 Second Drop Tower, 1,003 drops/22 investigations (this large number of tests was accomplished in spite of the fact that for five months the facility was undergoing a rehabilitation project); Zero-Gravity Facility, 153 drops and 113 normal gravity tests/13 investigations (this facility was unavailable for eight weeks due to system maintenance of supporting facilities and the unresolved budget issue which resulted in a labwide cutback of tests due to insufficient institutional support funds); Learjet, 113 flight hours comprised of 82 flights and 169 trajectories/8 investigations. Two experiments were also built up and successfully tested during a one week flight campaign on the KC-135 aircraft at the Johnson Space Center. This level of testing was also accompanied by a variety of design, build-up, assembly and check-out activities for many of the investigations. Some of the investigations supported in 1990 include the following: Cellular Flames, Droplet Combustion, Fuel Droplet Vaporization, Glovebox Experiments, Multiphase Flow, Interface Uniqueness, Spacecraft Fire Safety, Solid Surface Combustion, Particle Cloud Combustion and Gas Jet Diffusion Flames.

Several milestones were also reached in terms of upgrading the facilities of the Lewis Research Center through the Construction of Facilities (CoF) process. The Drop Tower underwent a Rehabilitation and Modification project. The major component of the effort was the addition of a new shop/build-up and testing area as well as several mechanical and electrical upgrades. The final design for the FY 91 discrete CoF project for the construction of the Space Experiments Laboratory (\$7.1 million, 38,000 square foot addition to the Zero-Gravity Facility) was completed. Construction is scheduled to be initiated in April of 1991. This facility will consist of a large number of laboratories, clean rooms, and a high bay area that will be utilized for the development, build-up and testing of flight and ground-based experiments. The design contracts for several CoF projects for the Zero-Gravity Facility were also completed. These include the rehabilitation of the below grade component of the facility and mechanical systems of the facility (FY91 projects) and the rehabilitation of the pumping systems (FY92 project).

The above-stated projects will help ensure that the ground-based facilities will continue to provide their vital role in support of the Microgravity Science and Applications Program by providing the baseline normal gravity and reduced gravity data needed to support the growing number of broad-based in-house and sponsored research studies.

Marshall Space Flight Center 105 Meter Drop Tube Facility

NASA Marshall Space Flight Center
Dr. Michael B. Robinson

During FY90, over 600 samples were processed in the MSFC 105 Meter Drop Tube Facility. Most of this number was in support of two joint activities between Vanderbilt University and MSFC. The investigators involved are Dr. Robert Bayuzick and Dr. William Hofmeister of Vanderbilt and Dr. Michael Robinson of MSFC. The first of these was an experiment from the flight program studying the effect of containerless processing on the nucleation of metals. In support of this program, the nucleation temperature of pure niobium samples was measured. It is intended to compare the nucleation temperatures from samples processed in MSFC facility to those found in both the Grenoble drop tube and the TEMPUS flight hardware. Other research was performed in support of a ground based study on the effect of undercooling on the microstructure and properties of niobium-based peritectic alloys. As part of the above two studies, a method was developed to measure the solidification velocity of samples after deep undercooling in the MSFC Drop Tube. This technique was applied to the samples of the above mentioned studies. Results have been compared to current dendritic solidification theory. Due to this research, modifications to the current solidification theories are being prepared.

In addition, research was conducted in support of the Center for Microgravity Research and Applications directed by T. Wang at Vanderbilt University. This effort involved adapting a furnace for the processing of metallic glass shells to the MSFC Drop Tube. The purpose of this study is to generate high-quality Inertial Confinement Fusion target-quality hollow spheres which have a high aspect ratio and are made of a low atomic number glass such as lithium borate.

APPENDIX A

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16. Abstract <p>This report is a compilation of the active research tasks for fiscal year 1990 sponsored by the Microgravity Science and Applications Division of the NASA Office of Space Science and Applications. The purpose of the document is to provide an overview of the program scope for managers and scientists in industry, university, and government communities. The report includes an introductory description of the program, the strategy and overall goal, identification of the organizational structures and people involved, and a description of each. The report also provides a list of recent publications.</p> <p>The tasks are grouped into several major categories: Electronic Materials; Solidification of Metals, Alloys, and Composites; Fluids, Interfaces and Transport; Biotechnology; Combustion Science; Glasses and Ceramics, Experimental Technology, Instrumentation, and Facilities; and Physical and Chemistry Experiments (PACE). The tasks cover both the ground-based and flight experiment programs.</p>					
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